













# SYSTEMATIC INORGANIC CHEMISTRY

FROM THE STANDPOINT  
OF THE PERIODIC LAW

A TEXTBOOK FOR ADVANCED STUDENTS

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## NOTE TO THE PRESENT EDITION

The text has been revised, and brought up to date by the incorporation of new material within the limits of the original space. The note on the stereochemistry of nitrogen has been replaced by accounts of the fixation of atmospheric nitrogen, and the use of liquid ammonia as a solvent.

The subject of radioactivity, which has made such rapid advances, receives rather more extended treatment than in the first edition of this book.

R. M. C.

G. D. L.

*March, 1911.*

**LIST OF THE ELEMENTS**  
**WITH THEIR SYMBOLS AND ATOMIC**  
**WEIGHTS (1911)**

**xvii**



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# LIST OF THE ELEMENTS (Cont.)

O = 16

Molybdenum	...	...	...	Mo	96.0
Neodymium	...	...	...	Nd	144.3
Neon	...	...	...	Ne	20.2
Nickel	...	...	...	Ni	58.68
Nitrogen	...	...	...	N	14.01
Osmium	...	...	...	Os	190.9
Oxygen	...	...	...	O	16.00
Palladium	...	...	...	Pd	106.7
Phosphorus	...	...	...	P	31.04
Platinum	...	...	...	Pt	195.2
Potassium	...	...	...	K	39.10
Praseodymium	...	...	...	Pr	140.6
Radium	...	...	...	Ra	226.4
Rhodium	...	...	...	Rh	102.9
Rubidium	...	...	...	Rb	85.45
Ruthenium	...	...	...	Ru	101.7
Samarium	...	...	...	Sa	150.4
Scandium	...	...	...	Sc	44.1
Selenium	...	...	...	Se	79.2
Silicon	...	...	...	Si	28.3
Silver	...	...	...	Ag	107.88
Sodium	...	...	...	Na	23.00
Strontium	...	...	...	Sr	87.63
Sulphur	...	...	...	S	32.07
Tantalum	...	...	...	Ta	181.0
Tellurium	...	...	...	Te	127.5
Terbium	...	...	...	Tb	159.2
Thallium	...	...	...	Tl	204.0
Thorium	...	...	...	Th	232.0
Thulium	...	...	...	Tm	168.5
Tin	...	...	...	Sn	119.0
Titanium	...	...	...	Ti	48.1
Tungsten	...	...	...	W	184.0
Uranium	...	...	...	U	238.5
Vanadium	...	...	...	V	51.06
Xenon	...	...	...	Xe	130.2
Ytterbium (Neoytterbium)	...	...	...	Yb	172.0
Yttrium	...	...	...	Y	89.0
Zinc	...	...	...	Zn	65.37
Zirconium	...	...	...	Zr	90.6





# INORGANIC CHEMISTRY

## CHAPTER

### THE ATOMIC AND MOLECULAR THEORIES

When two or more substances unite together to produce a third substance, as for example when copper unites with oxygen to form copper oxide, an examination of the nature and result of the change reveals certain qualitative and quantitative relationships between the interacting substances and the product or products of the reaction.

*Qualitatively*, adhering to the example stated, and supposing the change completed, the product of the operation is seen to differ in obvious properties, and in its relationships to other substances, from copper, which as a metal has disappeared, and from oxygen, which no longer exists in the system as a gas. Nevertheless, both copper and oxygen are obtainable from the product of their union by suitable processes of analysis.

A change has therefore occurred different from that procurable by a simple process of mixture, and it may be concluded that a more intimate state of union has been entered into. Moreover, the change from metal to oxide is not gradual but sudden, or at any rate takes place in well-defined stages; an intermediate stage consisting in the formation of a lower oxide of copper is possible in the case discussed, but what is true for the final is equally true for the intermediate stage. If the change is incomplete, a part of the copper will be found in the form of oxide, the remainder unchanged.

Material changes, such as that just described, are generally observed to be accompanied by the evolution or absorption of

energy in the form of heat, light, or electricity. When, for instance, copper and oxygen are brought together under conditions in which they combine spontaneously, a considerable amount of heat energy is evolved, so that less energy is present in the system after the change than before.

*Quantitative examination* of the action reveals regularities of a striking and far-reaching character. The evidence of the balance shows that the actual mass proportions in which the participants of the reaction combine is fixed, as well as the amount of the substance formed, no matter whether the oxide in question is produced directly or by an indirect process, and that from a given mass of the compound the same mass of each of the constituents may always be obtained by analytical processes. These facts depend firstly upon the law of the indestructibility of matter or conservation of mass, established by Lavoisier about 1770, and secondly upon the law of definite or constant proportion which was recognized as the outcome of a controversy between Berthollet and Proust in the years 1801 to 1808.

**Law of definite proportion.**—*The same compound always contains the same elements combined together in the same definite mass proportion; or, the masses of the constituent elements of every compound bear an unalterable ratio to each other, and to the mass of the compound formed.*

In the case under consideration 3·973 parts by weight of copper invariably combine with 1 part of oxygen to form 4·973 parts of black copper oxide.

The evolution of heat energy in such a combination as this is also susceptible of quantitative measurement, and for any particular reaction is constant in amount, the final result being the same in whatever way the reaction is brought about. For instance, when 3·973 grams of copper combine with 1 gram of oxygen gas heat equal to 23·25 K<sup>1</sup> is evolved.

When two substances combine, more than one product may result. If so, the mass proportions in which combination takes

<sup>1</sup> K = a large calorie, i.e. the amount of heat required to raise a gram of water from 0° to 100°.

place are simply related, being expressed by such ratios as 1 : 2, 2 : 3, and so forth.

Copper, for example, forms with oxygen a compound containing 7.946 parts of copper to 1 of oxygen, that is, exactly twice the proportion of copper contained in the previous compound.

If in any case a mixture of the two oxides were obtained and analysed, the proportion of copper present might be found to lie anywhere between the two extremes; and so it might appear that the composition of oxide of copper could vary within certain limits. A mistake of this kind was made by Berthollet, who on this account denied the law of definite proportions.

For instance, in the case of tin, two oxides are known in which the proportion of tin to oxygen is

7.44 : 1 and 3.72 : 1 respectively.

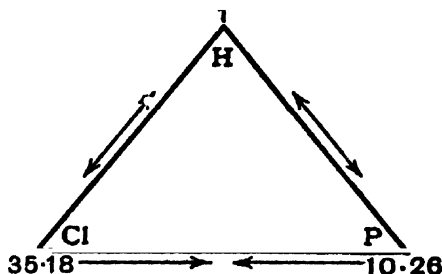
If a mixture of these two oxides were analysed the proportion of tin to oxygen would be found to be between 7.44 and 3.72. Proust, however, showed that the variation observed by Berthollet was due to the existence of mixtures in indefinite proportions of two compounds, each of definite composition; and as an outcome of the work of Proust and of Dalton the following law was established:—

**Law of multiple proportions.**—*When the same two elements combine together to form more than one compound, the different masses of one of the elements which unite with a constant mass of the other, bear a simple ratio to one another.*

If an element is known to combine separately with two other elements which also possess power of combination with each other, then further simple mass relationships present themselves. For instance, 1 part of hydrogen is found to combine on the one hand with 35.18 parts of chlorine, and on the other with 10.26 parts of phosphorus. Then it is found that 10.26 parts of phosphorus is the amount which will combine with 35.18 parts of chlorine; so that, considering these quantities as representing amounts of phosphorus and chlorine respectively which are “chemically equivalent” to 1 part of hydro-

gen, it may be said that amounts of these elements which are chemically equivalent to the same amount of a third element, are also chemically equivalent to each other.

This fact may be illustrated by the following diagram:—



The third law of chemical combination, of which the above instance is an illustration, may now be stated as follows:—

**Law of reciprocal proportions.**—*The masses of different elements which combine separately with one and the same mass of another element are either the same as, or simple multiples of, the masses of these different elements which combine with each other.*

The law of multiple proportions may also apply to the manner of combination of each pair of elements considered in the statement of the law of reciprocal proportions, as is provided for in it.

The facts of constancy of property and constancy of relative combining mass, which are made manifest by a study of the mutual actions of matter in bulk, form the basis of Dalton's atomic theory. This theory accounts for these facts by the doctrine of the atom; what is true for the bulk is supposed equally true for the ultimate individual particle; union known only in bulk is assumed to consist essentially of union between atoms or discrete individuals, which for a given substance are all alike and possessed of the same mass.<sup>1</sup> Consequently the mass relationships in which matter combines in bulk represent the mass relationships of the ultimate particles.

<sup>1</sup> It has been supposed by Crookes that the masses of the atoms of an element may vary within certain limits. If such variations exist they are exceedingly minute.

**The atomic theory may thus be stated:—**

(i) *Every element is made up of homogeneous atoms whose mass is constant.*

(ii) *Chemical compounds are formed by the union of the atoms of different elements in simple numerical proportions.*

The modern atomic theory differs from the atomic theory of the Greeks because it is made contingent on fact, and moreover serves as an instrument of investigation and discovery. It is a valuable working method, and not a mere intellectual hypothesis, like classical atomism. It is well to bear in mind that the atomic theory is based upon the experimental laws of chemical change, and cannot stand apart from them; and, further, that the theory does not concern itself with the ultimate nature of matter, still less with metaphysical speculations upon its reality, but with the units of chemical exchange. And, if it is argued that since modern discovery has proved that these units are not atoms in the etymological sense, therefore the atomic theory is discredited, it may be replied that they are real though divisible, and that discredit only results from pushing the theory beyond the limits of the experimental laws.

The atomic theory, thus experimentally deduced, serves as the basis of modern chemistry, and is therefore a fundamental doctrine second only in importance to that of the conservation of mass, upon which indeed it rests. The development of modern chemistry has been on the lines indicated by the theory, and each extension of chemical knowledge has served to amplify the theory.

An ultimate chemical individual, in the case of a particular substance, is either indivisible in a chemical sense,<sup>1</sup> that is to say, its division is a practical though not a theoretical impossibility, in which case the substance is an element; or else division is possible, and gives rise to new forms of matter, when the substance is a compound. In a study of the elements, or unresolvable components of matter, the first task demanded by Dalton's atomic theory is the determination of the relative

<sup>1</sup> The degradation of radio-active substances being considered for the time being as outside the limits of chemical change.

atomic masses which, as has been seen, are proportional to the masses in which the elements combine in bulk.

As a theoretical unit, the relative atomic mass or weight of hydrogen, specifically the lightest known substance, is taken.<sup>1</sup> If combination always occurred between one atom of each element concerned, the problem of atomic weight determination would be a simple one. The relative atomic weight in any case would be identical with the actual weight or proportion in which the element unites with, or is equivalent to, one part by weight of hydrogen. Dalton, indeed, assumed that the simplest manner of combination was always the real one, and devised arbitrary rules by which the number of atoms combining was in any case determined. Such a proceeding was unwarranted, no facts being then available by which true atomic weight values could be arrived at. Hence Dalton's atomic weights were really only chemical equivalents.

An element may indeed possess several simply related combining weights, in the sense of combining with one part by weight of hydrogen or its equivalent, in several proportions. For instance, in the compounds methane, ethylene, and acetylene, carbon possesses the combining weights 3, 6, and 12 respectively; and in the compounds ammonia, hydrazine, and azoimide, nitrogen possesses respectively the combining weights 4.6, 7, and 42. Similarly, carbon in union with oxygen, and many metals in union with oxygen or chlorine, possess more than one combining weight, because they form compounds in which the elements are united together in more than one proportion, according to the law of multiple proportions.

Thus the conclusion is arrived at that a certain number of atoms of one element may unite with a variable whole number of atoms of a second. The fact, therefore, that hydrogen and oxygen unite in approximately the proportions by mass of 1 : 8 gives no information as to the atomic weight of oxygen, which, if water is  $\text{HO}$ , as Dalton assumed, is 8; if  $\text{H}_2\text{O}$ , 16; if  $\text{HO}_2$ , 4;

<sup>1</sup> For practical purposes, however, it is more convenient to consider  $\text{O} = 16$ , so that  $\text{H} = 1.008$ . The International Committee upon Atomic Weights have decided upon this standard, and it is therefore adopted in the descriptive part of this book.

and so on. Further evidence is necessary to determine this atomic weight, and this evidence is found in the present and other cases by the consideration of the volume relationships in which gases combine.

That the properties of a gas may be referred to its constitution as a system of separate, mobile particles is readily accepted upon consideration of its properties of limitless expansion, adaptability of form, diffusion and solution in liquids.

**Gay-Lussac's law** that *gases combine with one another in simple proportions by volume*, and the corollary that *the densities of gases are simply related to their combining weights*, led to the hypothesis of an equal number of ultimate particles in equal volumes of gases under similar physical conditions. If these particles be atoms or ultimate individuals, the facts regarding the volume relations in combination as between hydrogen and chlorine or hydrogen and oxygen lead to the contradictory conclusion that the supposed indivisible atoms of hydrogen and chlorine in the first case and oxygen in the second have suffered division into two parts, since the volume of the resulting gas is in each case twice the volume which would result from pure synthesis of atoms.

Thus since

1 volume of hydrogen + 1 volume of chlorine give 2 volumes of hydrogen chloride, and

2 volumes of hydrogen + 1 volume of oxygen give 2 volumes of steam,

or

1 volume of hydrogen chloride is obtained from half a volume of hydrogen and half a volume of chlorine, and 1 volume of steam from 1 volume of hydrogen and half a volume of oxygen,

it is concluded that

1 compound atom of hydrogen chloride consists of half an atom each of hydrogen and chlorine, and that 1 compound atom of steam consists of 1 atom of hydrogen and half an atom of oxygen.

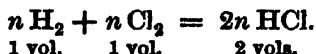
The introduction into the science by Avogadro of the idea of



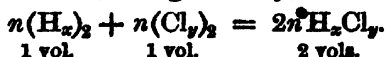
the molecule as a complex particle of a higher order than the atom, composed itself of atoms, alike in the molecule of an element, unlike in that of a compound, resolved this contradiction. The molecules of hydrogen, oxygen, and chlorine do suffer division into two parts, these parts then reuniting to form molecules of compounds. These facts and ideas find expression in **Avogadro's theory**,<sup>1</sup> which states that *equal volumes of all gases or vapours, simple or compound, contain, under similar conditions of temperature and pressure, equal numbers of molecules.*

This theory is substantiated by the kinetic theory of gases. Granting a fundamental and most probable assumption as to the nature of the motions of gas particles, and the effect of heat upon them, the purely dynamical reasoning of the kinetic theory demonstrates the truth of Avogadro's theory, and therefore of the views of chemical change between gases based on that theory.

An examination of the phenomena of union between hydrogen and chlorine gases now leads to the conclusion that equal volumes of hydrogen and chlorine, containing the same number of molecules, unite, giving twice that number of molecules of hydrogen chloride;  $n$  molecules of hydrogen and  $n$  molecules of chlorine give  $2n$  molecules of hydrogen chloride. The constituent atoms of each molecule of hydrogen have undergone separation and union with the atoms resolved from the molecules of chlorine. If now a molecule of hydrogen chloride is formed by the combination of 1 atom of hydrogen and 1 atom of chlorine, the conclusion follows that the molecules of these gases consist each of 2 atoms; thus:—

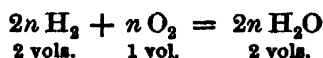


But the molecule of hydrogen might be  $\text{H}_4$ , and that of chlorine  $\text{Cl}_4$ , hydrogen chloride being  $\text{H}_2\text{Cl}$ , a relation satisfying the volumetric data; or, generally, the reaction might be



<sup>1</sup> This statement has passed beyond the region of hypothesis, and stands in the same category as the atomic theory. It is not a law, however, not being a summary of experimentally ascertained fact. ●

The assumption that a molecule of hydrogen chloride results from the union of 1 atom of each constituent is, however, the simplest, and accords with all known facts. The fact that only one compound of hydrogen and chlorine exists, and the more important fact that either hydrogen or chlorine can only be expelled from hydrogen chloride in one stage, furnish such a strong argument for this assumption as to make it exceedingly probable.<sup>1</sup> Indeed, if an atom be defined as the smallest particle which up to the present time has resulted from the resolution of a molecule, then these molecules must at present be considered to contain only 2 atoms, and are therefore written  $H_2$  and  $Cl_2$ . The molecule of oxygen is for similar reasons written  $O_2$ . Thus the equation



represents the formation of water, and the formula for a molecule of this substance being  $H_2O$ , the atomic weight of oxygen is 16.

## METHODS OF ATOMIC WEIGHT DETERMINATION

### I. *The Method of Vapour Density*

It was shown by Gay-Lussac that the combining weights of the simple gases are proportional to their densities; and as a consequence of Avogadro's theory it is further recognized that the molecular weights of all gaseous substances are proportional to their relative densities. If the density of a gaseous compound, referred to hydrogen as unity, be  $x$ , the molecular weight of the compound is  $2x$ , that of hydrogen being 2.

<sup>1</sup> The argument concerning the manner of displacement of elements from a compound is capable of extension. For instance, the hydrogen can be expelled from methane in four stages, the carbon in one. Therefore the formula for methane is  $CH_4$ , and the atomic weight of carbon 12.

Again, accepting the atomic weights of carbon and oxygen as 12 and 16 respectively, the empirical formula for acetic acid is  $CH_3O$ . The oxygen, however, may be expelled in two stages, thio-acetic acid being formed by the substitution of 1 atom of oxygen by sulphur. Therefore the molecular formula is probably  $C_2H_4O_2$ . And in general—When  $\frac{1}{n}$ th of the proportion of a constituent element in a chemical compound can be substituted, a molecule of the compound contains at least  $n$  atoms of that element. ●

Hence the problem of atomic weight determination resolves itself into ascertaining by analysis, where data are available, the smallest proportion by weight of an element which enters into the composition of a molecular proportion of the gas as indicated by the determination of its vapour density. An approximate value for vapour density is sufficient, accurate knowledge of a molecular weight being derived from analytical data when once the order of its magnitude is determined.

The molecular weight  $M$  of a compound  $A_xB_yC_z$  is equal to  $(xa + yb + zc)$ , where  $a$ ,  $b$ , and  $c$  are the atomic weights. The factors  $x$ ,  $y$ ,  $z$  must be whole numbers. The smallest proportion of an element ever found in a molecular proportion of one of its compounds is considered for the time being as the atomic proportion, and if the number of gasifiable compounds known is large, this value is very probably the atomic weight of the element. An example will make this clear.

Phosphorus forms a number of gasifiable compounds whose vapour densities have been determined, among which are phosphine, liquid hydride of phosphorus, phosphorous chloride, phosphoryl chloride, thio-phosphoryl chloride. A determination of the gas density of phosphine shows the molecular weight to be about 34; and by analysis 33.79 parts by weight of the compound contain 3.0 parts of hydrogen. Therefore the atomic weight of phosphorus cannot be greater than 30.79, though it may be a submultiple of this number. Similarly, the molecular weights and molecular proportions of phosphorus in the other compounds are the following:—

	Liquid hydride.	Phosphorous chloride.	Phosphoryl chloride.	Thio- phosphoryl chloride.
Molecular weight.....	65.58	136.33	152.21	168.15
Molecular propn. of P.	61.58	30.79	30.79	30.79

These figures make it probable that 30.79<sup>1</sup> is the atomic weight of phosphorus, since no molecular proportion of a compound is known to contain less than this amount of the element. At the same time the liquid hydride appears to contain 2 atoms of phosphorus, and to possess the formula  $P_2H_4$ .

<sup>1</sup> Or 31.04 if O = 16 and H = 1.008.

## II. *The Method of Specific Heat*

A means of fixing the atomic weight, depending on the previous determination of combining weight, and not involving a knowledge of the atomic structure of compounds, is afforded by the application of **Dulong and Petit's law** of atomic heats. In its widest sense the law asserts that *quantities of elements proportional to their atomic weights possess equal capacities for heat*, and fixes this constant heat capacity at 6.4, so that

$$\text{At. wt.} \times \text{sp. ht.} = 6.4; \text{ or } \text{at. wt.} = \frac{6.4}{\text{sp. ht.}}$$

The law thus implies an equal heat capacity for all atoms. It will be seen that in order to fix the atomic heat value so that the atomic weights calculated from it may be of the right order of magnitude, it is necessary for the atomic weight of some one element at least to be accurately established by independent evidence. The convergence of evidence from various sources gradually brought about a settled opinion as to the magnitude of atomic weight values of such well-known elements as copper and iron, and thus it was shown that the atomic weights calculated by Dulong and Petit, although inaccurate owing to faulty data, were of the right order of magnitude.

Strictly, the law is valid only for solid elements, generally metals, of atomic weights greater than 30.

The non-metallic elements of low atomic weight, to which must be added beryllium, an element of low atomic weight approximating in chemical character to the metalloids, display abnormal specific heats.

The specific heats of these elements all increase with rise of temperature, rapidly at first, and then more slowly until a maximum is reached at high temperatures.

Experimental determinations of the variation of specific heat with temperature have been carried out by Humpidge in the case of beryllium, and by H. F. Weber in the cases of boron, carbon, and silicon. The specific heat of beryllium is .3973 below 50°, increases with rise of temperature, and becomes

constant, and equal to about  $\cdot 62$  between  $400^{\circ}$  and  $500^{\circ}$ . The rates of variation with temperature of the specific heats of boron and carbon are similar to each other, and the values become constant at about  $1000^{\circ}$ ; the specific heat of boron at this temperature is about  $\cdot 50$ , and of carbon  $\cdot 46$ . A constant value,  $\cdot 203$ , is established for the specific heat of silicon at  $200^{\circ}$ . The products of these values and the accepted atomic weights of the three elements are approximately  $5\cdot 5$ ; and thus it is recognized that these elements have distinctly lower atomic heats than the metals. Sulphur and phosphorus also give values somewhat less than  $6\cdot 4$ .

The abnormality of specific heat of the above elements is probably due to differences in the molecular structure—and perhaps also in the arrangement of the constituent molecules in the mass—between them and the large majority of elements of constant atomic heat.

The absence of pronounced allotropism among the metals, and the monatomic constitution of the vapours of gasifiable metals, suggest a simple structure in the solid or liquid states; and conversely the molecular structure of the solid non-metals and metalloids is probably complex. It is observable, moreover, that, considering the series of elements of low atomic weight,  $\text{Li} = 7$ ,  $\text{Be} = 9$ ,  $\text{B} = 11$ ,  $\text{C} = 12$ , the atomic volumes<sup>1</sup> of Be, B, and C are the smallest of those of any of the elements, and that that of Li, as compared with them, is great. According to Mendeléeff, the magnitude of the atomic volume corresponds in a general sense to looseness of texture, or porosity in the solid element.

Thus the constituent particles of solid lithium are arranged with greater interspaces than is the case with boron and carbon, and approximate, therefore, nearer to the condition of the particles of a gas. If, now, in an element of low atomic volume the particles are both more complex, and more closely packed, the behaviour on heating may be explained as follows:—

The complexity and low degree of freedom of motion of the particles to some extent prevent the energy supplied in the

<sup>1</sup> See later, p. 32.

form of heat being transformed into motion both within and between the particles. A smaller quantity of heat therefore suffices to raise the temperature through a given number of degrees, and the specific heat is less than it would otherwise be. But at higher temperatures, owing to the increased freedom of both kinds of motion, more heat is required to raise the temperature of the substance, so that the specific heat increases, and the atomic heat approximates to the normal value.

Monatomic gases also have the minimum specific heat at constant volume; but this is due to simplicity, and not, as with the solids under discussion, to complexity of structure.

### III. *The Method of Isomorphism*

A third aid in fixing the correct multiple of the combining weight of an element which is to be received as its atomic weight is given by the phenomena of isomorphism, or similarity in crystalline form, which were first observed by Mitscherlich. In respect to its application to atomic weight determination, the law of isomorphism may be expressed in the following way:—*When in a given compound the replacement of one element by another does not alter the crystalline form of the compound, the element introduced is chemically analogous to the element replaced, and its compounds will be of the same type.*

A practical illustration of the use of the law by Mitscherlich and Berzelius will make clear its mode of application.

Sulphates contain the oxide  $\text{SO}_3$ , and chromates, being isomorphous with sulphates, must contain the oxide  $\text{CrO}_3$  instead of  $\text{CrO}_2$  as was previously supposed. Hence chromic oxide must be  $\text{Cr}_2\text{O}_3$ , and not  $\text{CrO}_3$ . The isomorphism of chromic and ferric salts necessitates the formula  $\text{Fe}_2\text{O}_3$  for ferric oxide, and consequently  $\text{FeO}$  for ferrous oxide. But magnesium, zinc, nickel and cobalt salts are isomorphous with ferrous compounds; hence their oxides must conform to the type  $\text{MO}$  instead of  $\text{MO}_2$  as previously supposed. The agreement of the atomic weights derived from this type with those indicated by Dulong and Petit's law justified the alterations which were thus made in the atomic weight values.

Another instance of the application of the law is furnished by the case of the element gallium. This metal forms an ammonium alum isomorphous with aluminium ammonium alum  $\text{Al}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ . The sulphate of gallium is therefore probably  $\text{Ga}_2(\text{SO}_4)_3$ , and the oxide  $\text{Ga}_2\text{O}_3$ , whence, the equivalent being 23, the atomic weight is 69. This value is confirmed by other considerations.

A careful examination of the isomorphism of the salts of the alkali metals has been made by Tutton. Thus the replacement of potassium in potassium sulphate by rubidium and caesium respectively does not alter the crystalline form of the sulphate, though the thermal and optical properties of the crystals undergo slight changes, generally varying in amount in the same sense as the variation in the atomic weights of the metals. The identity of crystalline form of the sulphates confirms the chemical similarity of the three metals, and harmonizes therein with the analogies revealed by the study of their chemical behaviour.

True isomorphous compounds may form mixed crystals when a solution of a mixture of the salts is allowed to crystallize, or a crystal of a compound may induce crystallization in a supersaturated solution of an isomorphous substance, as in the case of the alums.

Equality in the number of atoms in the molecule of a compound, together with an apparent similarity in structure, may be accompanied by isomorphism; thus  $\text{NaNO}_3$  is isomorphous with  $\text{CaCO}_3$  in calc spar, and  $\text{KNO}_3$  with  $\text{CaCO}_3$  in aragonite.

The actual structures  $(\text{Na}, \text{K})\text{ONO}_2$  and  $\text{Ca} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{CO}$ , as well as the chemical behaviour, are, however, widely different. Only when isomorphism can be shown to be a true sign of similarity of molecular structure and general chemical behaviour, as for example in the case of the salts  $\text{KClO}_4$  and  $\text{KMnO}_4$ , may it be used as evidence in atomic-weight determination.

Further, the deductions from isomorphism are liable to be obscured by the property of polymorphism; this is illustrated

by the dual crystalline structure manifested by calcium carbonate, and also by silica in quartz and tridymite, as well as by the existence of two crystalline modifications of sulphur, and four of ammonium nitrate.

### VALENCY

The molecular composition of many gasifiable binary compounds, containing only one atom of one of the constituent elements, shows that a single atom may combine with more than one other atom, a conclusion also to be drawn from the data of the law of multiple proportions.

The following series of gasifiable binary compounds, whose molecular composition may be arrived at by the application of principles studied above, serves as an illustration:



From this series it is possible at once to form a conception of valency, or saturation or combining capacity, in the narrower sense, as expressing the largest number of other atoms with which the atom of a given element is known directly to combine.

Thus, for instance, from the above, the valency of sulphur appears to be two, that of nitrogen three, carbon four, phosphorus five, and tungsten six.

No binary compound in which 1 atom of hydrogen combines directly with more than 1 atom of another element is known;<sup>1</sup> therefore, as regards combining capacity or valency, hydrogen represents the lower limit, and is designated mono- (or uni-) valent.

The existence of the gas molecules HF, HCl, HBr, HI shows that the elements fluorine, chlorine, bromine, and iodine may also behave as monovalent; accordingly these elements are also employed as standards in the determination of valency.

One atom of an element never combines with more than 4 atoms of hydrogen (*e.g.*  $\text{CH}_4$ ,  $\text{SiH}_4$ ). Higher valency is shown in the halogen compounds, and therefore a distinction

<sup>1</sup> In  $\text{N}_2\text{H}$  only 1 nitrogen atom is attached directly to hydrogen.

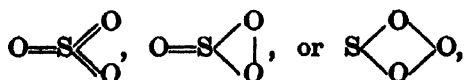


must be drawn in practice between hydrogen and halogen valency; for example, the highest hydrogen valency of phosphorus is three, in  $\text{PH}_3$ , and the highest halogen valency is five, in  $\text{PF}_5$  and  $\text{PCl}_5$ .

The recognition of this distinction raises the question whether valency can be considered to be an inherent property of an atom. It is true that valency is only known in its manifestations, but a consideration of all the types of compound which an element forms, generally leads to a definite conclusion as to the maximum valency which it can exert. The sum of the properties of an element, including the types of its compounds, is shown in the position which it occupies in the periodic system (*q.v.*). Hence the periodic system may be appealed to for an indication of the potential valency which is an inherent property of an element.

Nevertheless this system sometimes indicates a higher potential valency than is ever realized. Iron, cobalt, and nickel, for instance, are not known to be octavalent, nor is fluorine ever heptavalent, as the periodic law indicates. Likewise the divalency of copper and trivalency of gold are anomalous from this point of view.

In the determination of the valency of a given element it should be remembered that the only direct and rigorous experimental evidence is afforded by a knowledge of the molecular weight and composition of a gasifiable compound, containing 1 atom of the element under discussion united to standard monovalent atoms. For instance, no indisputable conclusion as to the valency of sulphur can be drawn from the molecular weight and atomic composition of  $\text{SO}_3$ , the constitution of which may be represented in three ways,



in which sulphur is respectively hexa-, tetra-, and divalent. The chemical behaviour of the compound, however, makes it unlikely that it contains a chain of oxygen atoms; hence the conclusion that in  $\text{SO}_3$  sulphur is hexavalent, a conclusion

which is fully upheld by the periodic law, and has recently been confirmed by the preparation of sulphur hexafluoride,  $\text{SF}_6$ .

A knowledge of the atomic weight of calcium, again, leads to the formulæ  $(\text{CaO})_n$  and  $(\text{CaCl}_2)_n$  for the oxide and chloride respectively; but whatever may be the real molecular magnitudes of these compounds, their composition is represented by the formulæ  $\text{CaO}$  and  $\text{CaCl}_2$  with as much accuracy as present knowledge affords. Calcium is accordingly regarded as divalent; and here also the periodic law affords testimony to the correctness of this conclusion.

Some complication of the simple facts of valency arises from the display by many elements of varying valency; for example, by tin in  $\text{SnCl}_2$  and  $\text{SnCl}_4$ , by iron in  $\text{FeCl}_2$  and  $\text{FeCl}_3$ , by phosphorus in  $\text{PCl}_3$  and  $\text{PCl}_5$ , and by tungsten in  $\text{WCl}_4$ ,  $\text{WCl}_5$  and  $\text{WCl}_6$ . A number of elements exhibit valencies which, increasing or diminishing by two, are always either odd or even, and formerly it was thought that a regularity of this kind existed which might be called a law. Such is not the case, numerous examples of increase or decrease by single units being known. The group valencies indicated by the periodic law are, however, seldom if ever exceeded, and these therefore indicate the maximum values for the various groups of elements. It must nevertheless be remembered that the manifestation of valency is contingent upon chemical combination; whenever union occurs, valency must come into operation as a measure of its extent. Active valency is not, therefore, a constant property like atomic mass; indeed it has been well compared to the force of friction, which is only called into play by external causes, and which may vary from zero to a certain maximum.

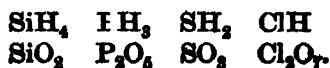
The existence of the so-called "molecular compounds" raises a difficult question. This term was formerly applied to substances whose structure was inexplicable on the ordinary laws of fixed valency; salts containing water of crystallization, double salts such as the alums, and complex salts such as ferrocyanides and chloroplatinates serve as illustrations.

The special application of the term "molecular compound"

implies a difference in the nature of the union of the constituent atoms to that obtaining in an ordinary compound. This distinction is unwarranted by the facts. Salts like the chloroplatinates—or platinichlorides—and the ferro- and ferricyanides exist in solution, and therefore contain complex ions, so that the mode of union within them must be considered to be atomic; and from these compounds to the alums and other double salts, which are more or less decomposed by water, all stages of stability exist. Moreover, molecular compounds may enter into reactions of double decomposition or metathesis; thus triethylammonium tribromide, which might be considered a molecular compound of triethylamine and bromine, reacts with potassium iodide, as shown by the equation  $(C_2H_5)_3NBr_3 + 3 KI = (C_2H_5)_3NI_3 + 3 KBr$ ; and the five molecules of water of crystallization in  $CuSO_4 \cdot 5 H_2O$ , are successively replaceable by ammonia, with the ultimate formation of  $CuSO_4 \cdot 5 NH_3$ . Analogous phenomena are abundantly provided by the "ammines" and allied compounds of the metals of the eighth group of the periodic system, and the chemical changes and transpositions which these substances undergo are characteristic of normal chemical compounds. Many molecules which are generally considered saturated, *e.g.*  $C_2H_4O_2$  and  $HF$ , and even  $H_2O$ , are known to polymerise;  $(C_2H_4O_2)_2$  and  $(HF)_2$ , indeed, can exist in the gaseous state.

There is no intrinsic difference, therefore, between the ordinary and the molecular compound, except that the latter generally undergoes dissociation more readily than the former. The development of higher valencies must consequently be assumed in order to account for these compounds; and the question arises as to what further justification there is for this assumption.

Now it may be observed that the sum of the maximum hydrogen and oxygen valencies of elements in certain groups of the periodic system is equal to eight. The following series of compounds illustrates this fact:—



According to Abegg,<sup>1</sup> every element possesses a maximum valency of eight, made up of positive and negative components, or normal and contra-valencies. These are composed as follows, taking a single series for illustration:—

	Na	Mg	Al	Si	P	S	Cl
Normal valencies...	+1	+2	+3	} $\pm 4$ {	-3	-2	-1
Contra-valencies....	-7	-6	-5		+5	+6	+7

The contra-valencies are latent in the first three elements of the series; and the quality of the valency manifested by a particular atom depends on the character of the element or group with which it is associated. Thus chlorine manifests a single negative valency towards hydrogen or metals, and a maximum positive valency of seven towards oxygen.

The relative strengths of the two kinds of valency depend upon the chemical nature of the atom itself. Thus the alkali metals are too electropositive to show negative valencies, and fluorine is too negative to exhibit positive valencies; that is to say, it cannot combine with oxygen.

Latent contra-valencies may, however, become operative under certain circumstances, and thus "molecular compounds" are accounted for, the instability of these compounds in many cases being due to the weakness of the contra-valencies to which they owe their existence.

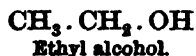
The conception of atomic valency is profitably extended so as to include compound radicles. This may be done, as has been shown by Mendeléeff, by the application of the third law of motion, that action and reaction are equal and opposite. Thus the molecule  $\text{H}_2\text{O}$  is a system in equilibrium, and therefore not only do  $\text{H}_2$  and O exert an equal and opposite force upon one another, and are therefore chemically equivalent, but the same is true of H and OH, so that OH is a monovalent radicle. Similarly,  $\text{CH}_3$  is monovalent because it maintains equilibrium with a single hydrogen atom in  $\text{CH}_4$ . The same conclusion is of course arrived at by considering OH and  $\text{CH}_3$  as displacing one atom in a molecule of hydro-

<sup>1</sup> *Zeitschr. Anorg. Chem.* xxxix. 330 (1904).

gen,  $H_2$ . Further, since  $OH$  and  $CH_3$  are monovalent radicles, and equivalent to a hydrogen atom, they should unite together in pairs, and with each other, as hydrogen atoms do; thus the probable existence of hydrogen peroxide  $HO.OH$ , ethane  $CH_3.CH_3$ , and methyl alcohol  $CH_3.OH$  may be predicted.

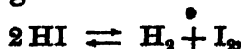
Further consideration of these two radicles as equivalent to a hydrogen atom will account for the compounds  $HO.Cl$ ,  $(HO)_3As$ ,  $CH_3.Cl$ ,  $(CH_3)_2O$ ,  $(CH_3)_2CH_2$ ,  $(CH_3)_3CH$ ,  $(CH_3)_4C$ .

The recognition of compound radicles, and the principles underlying their combination, contributed very largely to the development of organic chemistry. Thus, for example, Kolbe recognized that a hydrogen atom might be replaced by a methyl group, as, for instance, in methyl alcohol,  $CH_3OH$ , and this led to the discovery of secondary and tertiary alcohols, as the following:—

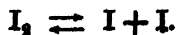


### PHYSICAL CAUSE OF VALENCY

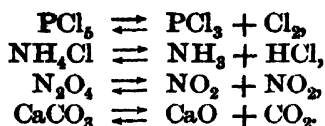
Van't Hoff has shown that valency may depend on two factors; firstly on the form of the atom, and secondly on the state of motion of the component atoms of the molecule. If an atom is not spherical, each departure from the spherical form will produce a centre of attraction, that is, a unit of valency, in a given direction, since a second atom may approach the first more nearly in that direction. The amplitude of the atomic vibrations will also determine the valency actually manifested, for the greater the amplitude the less the influence of attraction to a given point, and the less the chance of union, and *vice versa*. In illustration, reference may be made to the effect of temperature on hydriodic acid. Below  $200^\circ$  this compound begins to dissociate thus:—



and at  $1700^\circ$  iodine itself dissociates thus:—



Other cases of dissociation are shown in the equations:



At a sufficiently high temperature no doubt all compounds would be resolved into simple atoms of their constituents, and combining capacity or active valency would be zero.<sup>1</sup> On cooling, combination would again ensue, with the production of gas molecules, stable between certain limits, whose composition affords the existing experimental data of valency. Below the lower limit, new combining capacities may appear, even in the gaseous state, as in the case of  $(\text{HF})_2$ ,  $\text{N}_2\text{O}_4$ , and  $(\text{C}_2\text{H}_4\text{O}_2)_2$ . In the liquid and solid states the molecule is still more complex. In the broader sense, therefore, valency must be admitted to vary within wide limits, until in solids and liquids it merges in the force of cohesion.

When under comparable physical conditions an element displays more than one valency, the compound of lower valency is almost invariably capable of conversion into one corresponding with the higher type, so that a saturated compound is produced. For instance, trivalent nitrogen in ammonia becomes pentavalent in ammonium salts, divalent iron in ferrous chloride becomes trivalent in ferric chloride, and divalent carbon in carbon monoxide becomes tetravalent in carbon dioxide and carbonyl chloride.

The valency discussed in the preceding paragraph is active and not potential valency. With reference to carbon, a large number of compounds are known which are unsaturated, but, with the exception of the case quoted above, the property of unsaturation is connected with the mode of union of a carbon atom with a neighbouring carbon or other atom, so that no single unit of valency remains unsaturated, but each of two

<sup>1</sup> The simpler composition of the hotter as compared with the cooler stars justifies the opinion that at a sufficiently high temperature the atoms of the known elements are resolved into simpler constituents.

adjacent atoms possesses one or two unsaturated units. Examples of such compounds are  $C_2H_4$ , which can unite with two, and  $C_2H_2$ , which can unite with four hydrogen or halogen atoms. Kekulé, who developed the ideas of valency as applied to the carbon atom, assumed that the valency of this element is always equal to four; and in accordance with this assumption, the above compounds receive the following graphic formulæ:—



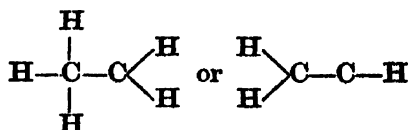
in which double and triple bonds appear between the carbon atoms, each bond representing a unit of valency.

Now it might be supposed that the active valencies of the carbon atoms in these compounds are three and two respectively, according to the formulæ:



since these atoms are respectively united to three and two other atoms; and the analogy of other elements supports this view. Moreover, as has been seen, the idea of constant active valency cannot be maintained in the case of other elements.

Such a view might be accepted for practical purposes, were it not that the supposed latent valencies of the two carbon atoms in these compounds are not independent, so that such bodies as



cannot be produced, the satisfying of one or more valency-units of one atom always involving its neighbour to the same degree, so that such compounds as  $CH_3 \cdot CH_3$  or  $CH_3 \cdot CH_2Br$  are produced from  $C_2H_4$ .

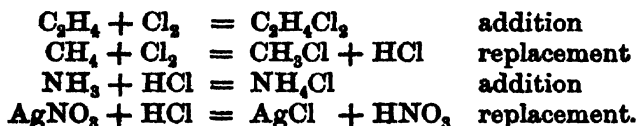
It may be that such manner of saturation expresses a law of molecular symmetry, but the fact itself should be recognized

in the manner of formulating the unsaturated compound. Further, the mode of union of two unsaturated carbon atoms in a molecule differs from that of saturated atoms, since on oxidation of an unsaturated compound rupture takes place always at the point of unsaturation. These facts are not recognized by regarding some valencies as latent, but are met by the theory that the otherwise inoperative valencies are the cause of the phenomena. Thus the modified union of carbon atoms in unsaturated compounds is expressed by double and triple bonds, the valencies of carbon being thus constantly represented as four.

An advantage of this view is that it accords with the principles underlying the stereo-chemical theory of the carbon atom, to which brief reference will shortly be made, and which postulate the tetravalency of the carbon atom in all compounds.

It must not, however, be supposed that double or triple is stronger than single union; the opposite is the case. Consequently no mechanical significance must be attached to "bonds".

The compounds of lower valency type, in which the combining capacity of the nuclear atom or atoms is not fully satisfied or "saturated", are distinguished from compounds of maximum valency type by entering into reactions of direct addition, whilst the latter can only participate in reactions of replacement. The following are examples of these two classes of reaction:—



The method of graphic formulæ employed above for indicating the internal structure of molecules, the atoms being represented as linked together by bonds signifying units of valency, is of wide application. It is of special value in organic chemistry for showing the probable structure of a

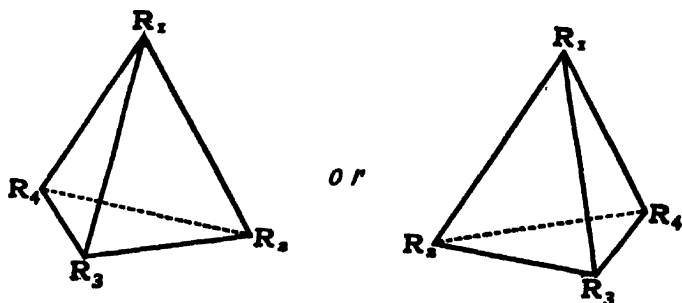


compound as deduced from its synthetic and analytic reactions, and it is also widely employed in inorganic chemistry though often with less exact significance.

A graphic formula serves to refer a given compound to a simpler type from which it may be derived by chemical processes; to suggest relationships to other compounds into which it may be transformed by such processes; and to indicate certain typical reactions which it may be expected to show.

Finally, graphic formulæ have a spatial significance to which brief reference will here be made.

Taking a compound of the type  $CR_1R_2R_3R_4$ , the four monovalent radicles may be regarded as grouped about the carbon atom, occupying definite mean positions. Unless all the groups lie in one plane with the carbon atom, a tetrahedral arrangement results, the groups  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  forming the apices of the tetrahedron. Using the regular form for simplicity, the spatial configuration becomes:—



The solid figures thus indicated are "asymmetric", possessing no plane of symmetry, and although they represent compounds of the same composition, they are not identical, being non-superposable, and are related to one another as object and image, or as a right-handed and a left-handed screw. It may be expected, therefore, that two compounds of the composition  $CR_1R_2R_3R_4$  will exist which will differ from one another in some such subtle manner as is suggested by the geometrical formulæ. This is the case. Crystals of such compounds are related to one another as object and image, and are said to

be *enantiomorphous*; and when transparent, such substances, whether in solution or not, are optically active, rotating the plane of polarized light, in the case of one compound to the right to a certain extent, and in the case of the other to an equal extent to the left. In all their chemical and many of their physical properties they are, however, identical.

The foundations of the principles of "stereo-chemistry", or chemistry in space, were laid by Pasteur, van't Hoff, and le Bel. This study has recently been extended to elements other than carbon, such as nitrogen, sulphur, tin, silicon and phosphorus.

The above considerations leave almost untouched the question of the ultimate nature of valency, which is probably connected with that of matter itself.

The idea that chemical affinity is essentially electrical was first brought forward by Humphry Davy, and received support later from the laws of electrolysis discovered by Faraday. Thus an ion carries a definite charge of electricity, the magnitude of which is always a multiple of a certain unit, but depends upon the valency of the atom or group constituting the ion. So it is concluded that electricity is atomic like matter. The unit or atom of electricity is called an electron; and we know that electrons are produced by the disintegration of radio-active substances, and therefore are a constituent of matter. An interesting theory of valency, which we owe to Ramsay,<sup>1</sup> suggests that electrons, partially separated from the atoms of matter, form the bonds of chemical affinity between them, and thus constitute units of valency.

<sup>1</sup> *Chem. Soc. Trans.*, xciii (1908), 778. For a review of the whole subject of valency see J. N. Friend's book entitled *The Theory of Valency*.

## CHAPTER II

## CLASSIFICATION AND THE PERIODIC LAW

The vast mass of experimental data of chemistry only becomes systematic when the elements and their compounds are classified. The nature and aim of classification have been set forth by Huxley in the following words:—

“By the classification of any series of objects is meant the actual or ideal arrangement together of those which are alike, and the separation of those which are unlike; the purpose of this arrangement being primarily to disclose the correlations, or laws of union, of properties or circumstances, and secondarily, to facilitate the operations of the mind in clearly receiving and retaining in the memory the characteristics of the objects in question”.

The establishment of an inductive law in the experimental sciences involves the following sequence of logical operations:—

- I. Induction.
- II. Verification.
- III. Deduction (or Discovery).

By the inductive process the law receives its statement, which is an expression of the common features presented by the observed facts; in the process of verification it must be shown that the law is capable of embracing within its scope other facts as they become known; and by the third or deductive process the availability of the law as an instrument of discovery is tested, and thus new facts or relationships of facts are discovered.

The rise and development of the periodic law as an instrument for the systematic study of the elements, as it is traced in the sequel, will be seen to correspond with and fulfil each of these requirements.

Before proceeding to the exposition of the law, it may, however, be well to glance briefly at some earlier attempts at

classification of the elements. Of these the most important was the electro-chemical classification of Berzelius. According to him every atom was the bearer of fixed electrical charges, both positive and negative, and as these differed in relative magnitude, displayed either a positive or negative electrical "unipolarity"; metallic atoms bore an excess of positive, non-metallic atoms an excess of negative electricity. Combination between atoms was resultant upon the partial satisfaction of their respective charges, the electrical character of the resulting product depending upon the nature of the unsatisfied residue. Thus, in potassium oxide, the positive charge of the potassium not being fully satisfied by the negative charge of the oxygen, a balance of positive charge remained; whilst in sulphur trioxide a balance of negative electricity was present. Combination could therefore ensue between these oxides, yielding potassium sulphate, which still bore a positive residue and was therefore able to unite with aluminium sulphate, which bore a negative charge, to form alum. Union would thus occur in the first instance between atoms, then between binary compounds, and so forth. Berzelius was able to classify the elements in a series in which the gradation with respect to electric character was from positive to negative, which is equivalent to a transition from metal to non-metal; and the electrical method of union, related to this classification, formed the basis of the dualistic theory of chemical compounds, which for some time held the field.

It will be perceived that the electro-chemical views of Berzelius are the historical predecessors of our modern doctrine of ionic dissociation, according to which a dilute solution of an electrolyte (an acid, base or salt) contains ions which are the bearers of positive or negative charges. Thus potassium chloride is regarded as existing in dilute aqueous solution in the state of dissociated ions  $\overset{+}{K}$  and  $\bar{Cl}$ , potassium sulphate in the state of ions  $2\overset{+}{K}$  and  $\bar{SO}_4$ , and so forth.

The value of the electro-chemical behaviour and its correlated properties in the study of the chemical character of an element

will again be referred to in discussing the periodic variation of the chemical properties of the elements.

Regularities between the atomic weights of the elements were remarked prior to the general statement based on them by Mendeléeff. Döbereiner, for instance, pointed out that the atomic weights of allied elements were either very nearly equal, or separated by regular intervals. Thus iron, cobalt, and nickel formed a triad of elements with nearly equal atomic weights, and lithium, sodium, and potassium a triad whose atomic weight differences  $\text{Na} - \text{Li}$  and  $\text{K} - \text{Na}$  were approximately equal to 16.

The first attempt at a complete classification based on atomic weights was made in 1864 by Newlands, who enunciated the principle of periodicity in his "law of octaves". By arranging the elements in the order of their atomic weights, he was able to demonstrate the general validity of his statement that "the eighth element, starting from a given element, is a kind of repetition of the first, like the eighth note in an octave of music".

The periodic law, however, first received its full statement, in 1869, by Mendeléeff, and it may be expressed as follows:—  
*"The physical and chemical properties of the elements and their compounds are periodic functions of the atomic weights"; or, "If the elements are arranged in order of increasing atomic weight, their properties vary in a definite manner from member to member of the series, but return more or less nearly to the same value at certain fixed points in the series".*

This fundamental proposition serves as the basis of modern classification. In 1870 Lothar Meyer also drew attention to the periodic relationship between certain physical properties of the elements and their atomic weights.

Excluding hydrogen, for which there is no known analogue, and leaving out of consideration for the present the recently discovered inert gaseous elements, lithium is the starting-point of the following series of seven elements:—

Li    Be    B    C    N    O    F,

in which the change of chemical character is from metallic (positive) to non-metallic (negative). Following fluorine is sodium, the analogue or "octave" of lithium, and forming the starting-point of the series or period,

Na    Mg    Al    Si    P    S    Cl,

each member of which is the analogue of the correspondingly situated element of the first period.

From potassium, which follows chlorine, the analogue rubidium is not reached until a longer period of seventeen elements has been traversed,

K    Ca    Sc    Ti    V    Cr    Mn    Fe    Co    Ni  
Cu    Zn    Ga    Ge    As    Se    Br  
Rb

The set of three elements, Fe, Co and Ni, links the first seven elements with the last seven, and these two series contain, in corresponding positions, as shown, elements which are allied to one another, and to the corresponding members of the first or short periods.

The second long period is complete, except for an analogue to manganese, and runs:

Rb    Sr    Y    Zr    Nb    Mo    —    Ru    Rh    Pd  
Ag    Cd    In    Sn    Sb    Te    I

Placing hydrogen alone as series one, and dividing the long periods into two series comprising the first seven and last seven members, the three central members being omitted, the elements become arranged into seven groups, each group after series three containing two sets of elements which form sub-groups, A of the elements of even series, B of uneven series. The transitional triads of the long periods then fall into Group VIII. (See diagram on following page.)

The allocation of the members of the two short periods into sub-groups A and B is somewhat arbitrary, on account of the fact that these elements display many anomalous relationships

THE PERIODIC SYSTEM—TABLE I

GROUPS	O'	I	II		III		IV		V		VI		VII	VIII
SUB GROUPS		A	B	A	B	A	B	A	B	A	B	A	B	
SERIES 1		H	Increase in oxygenic properties →											
"	2	He	Li	Be	B	C			N		O		F	
"	3	Ne	Na	Mg	Al	Si			P		S		Cl	
"	4	Ar	K	Ca	Sc	Ti	V	Cr		Mn				Fe Co Ni
"	5		Cu	Zn	Ga	Ge		As	Se				Br	
"	6	Kr	Rb	Sr	Y	Zr	Nb	Mo						Ru Rh Pd
"	7		Ag	Cd	In	Sn		Sb	Te				I	
"	8	Xe	Cs	Ba	La	Ce (Pr) (Sm) (Eu) (Gd) (Tb) (Yb)								
"	9													
"	10													
"	11		Au	Hg	Tl	Pb	Ta	W						Os Ir Pt
"	12			Ra		Th		U						

NOTE.—In connecting Ba and Ta through the rare earth metals, Benedicks proposes (*Zett. Anorg. Chem.* xxxix (1904), 41) to unite Series 8 and 10 in one, and thus obliterate Series 9, which contains no elements. In this arrangement, and disregarding Series 1, there remain only eight blank spaces in the periodic diagram.

to their group successors, just as do the first members of homologous series in carbon compounds. They summarize the properties of the group, however, and are called by Mendeléeff "typical elements". In referring them to sub-groups, it is perhaps best to be guided by the natural relationships; thus it is more reasonable to refer sodium to sub-group A containing the alkali metals, than to sub-group B; though chlorine is evidently to be classed with bromine and iodine in the latter sub-group; and, in general, relationship to the elements of sub-group B becomes closer towards the end of each short period.

After the second long period, the remaining series are incomplete, elements which would fill the blank spaces being unknown. It might be thought that the disposition of the remaining elements with blank spaces is artificial; but the completed periods demonstrate the validity of the law, and the relationships of the remaining elements to the individual members of these periods determine the positions of the elements. Thus, for instance, tungsten is placed in Group VI A, and in the tenth series, on account of its analogy to molybdenum and its atomic weight.

In order that the law may be fully established, it is necessary not only that the elements shall fall into groups, but also that the series when complete shall not be interfered with; for instance, no element can be discovered which may be interposed between boron and carbon without invalidating the law. It is further necessary that the nature of the change of property in passing from member to member shall be uniform throughout the series.

The atomic-weight differences in a group are remarkably constant. In the first two periods this difference is approximately 16, as between Na and Li, S and O, Cl and F. With the elements of higher atomic weight the difference is approximately 46, as between Rb and K, Sr and Ca, Sb and As.

It will now be shown how the periodicity is illustrated by the physical properties of the elements, and then in what manner the chemical characters vary.



## PHYSICAL PROPERTIES

*Density.*—The densities of the elements in the solid state vary periodically with the atomic weights, as is shown by the following series:—

Na	Mg	Al	Si	P	S	Cl <sup>1</sup>			
·97	1·75	2·67	2·49	1·82 to 2·34	1·91 to 2·07	1·33			
K	Ca	Sc	Ti	V	Cr	Mn			
·87	1·55	2·5 (?)	4·87	5·5	6·92	7·42	Fe	Co	Ni
Cu	Zn	Ga	Ge	As	Se	Br	7·8	8·5	8·8
8·93	7·15	5·96	5·47	5·4 to 5·9	4·26 to 4·8	2·97 <sup>1</sup>			

It will be noticed that the density varies in a regular manner from member to member of the series, reaching a maximum in the central members; it also increases with increase of atomic weight in a group.

*Atomic volume.*—A more comparable magnitude than the density is the atomic volume; this is the ratio of the atomic weight to the density, and is denoted by the symbol  $V$ , or  $A V$ . This value cannot be expressed absolutely, the actual figures representing the volume in cubic centimetres of an atomic proportion in grams (the gram-atom).

The variation in this magnitude is shown at a glance by Lothar Meyer's curve of atomic volumes, in which atomic weights are plotted as abscissæ and atomic volumes as ordinates (see diagram opposite). The members of each period occupy successive positions on the curve, and those of each group occupy similar positions. In the first portion of the curve, containing elements of lowest atomic weight, an anomaly occurs in the relative positions of helium and lithium. According to Onnes<sup>2</sup>, the density of liquid helium is only 0·15; thus its atomic volume is 26·6, whilst that of hydrogen is 1·44, and that of lithium 13. Thus the curve, ascending steeply from hydrogen to helium, descends again through lithium to beryllium; and so, unlike the other alkali metals, lithium does not

<sup>1</sup> Densities in liquid state.

<sup>2</sup> *Proc. K. Akad. Wetensch. Amsterdam* (1908), 10, 744; 11,

occupy an apex. This is another example of anomalies presented by so-called "typical" elements. Certain portions of the curve are incomplete owing to uncertainty of data concerning the metals of the rare earths, and also on account of undiscovered elements.

It will be noticed that the elements of the alkalis occupy the maximum points, the central elements—in the long periods those of the transitional triads—occurring at the minima.

The manner of variation of atomic volume with rise of atomic weight in a group is shown by the line joining the members of a group on the successive curves.

In some cases the atomic volume increases with increase in atomic weight, as in the phosphorus group, but particularly in the group of alkali metals. In the halogen family the atomic volume is constant, and also in the triads of Group VIII.

(According to Mendeléeff, the relative magnitudes of the atomic volumes are connected with the chemical activity of the elements, since they roughly measure the size of the intermolecular spaces, or "porosity" of structure. An element of high atomic volume, or loose texture, such as an alkali metal, may be expected to display greater chemical activity than one of low atomic volume, or dense texture, such as a member of Group VIII.)

*Atomic volume of Oxygen in Oxides.*—The quotient molecular weight divided by density gives the molecular volume (MV) of a compound. If the atomic volume of an element in its oxide be supposed to be the same as in the free state, and the atomic volume of oxygen in it be calculated by subtracting the atomic volume of the other element from the molecular volume of the oxide, remarkable periodicity in the former value is revealed.

From the relation  $V(O) = MV(Na_2O) - 2V(Na)$ ,

$$V(O) \text{ in } Na_2O = 27.6 - 47.2 = -19.6;$$

$$\text{and further } V(O) \text{ in } SO_2 = \frac{40.6 - 15.5}{3} = +8.4,$$

$$\text{whilst } V(O) \text{ in } Al_2O_3 = \frac{26.2 - 20.1}{3} = +2.0.$$

The atomic volume of oxygen in an oxide varies periodically with the nature of that oxide; it changes from negative in the alkali oxides to nearly zero in the oxides of dual chemical character, like  $\text{Al}_2\text{O}_3$  and  $\text{SnO}_2$ , of Groups III and IV, and to positive in the acidic oxides of Groups VI and VII, and in those of the transitional periods and their immediate successors.

Those oxides, therefore, in which the volume of oxygen is negative are basic, and those in which it is positive are either easily reducible or acidic.

*Melting point.*—The melting-points of the elements also vary periodically with the atomic weights.

(Elements at or immediately preceding minima in the atomic volume curve have high melting-points, e.g. B, C, Si, the metals of Group VIII, which are at minima, and Ti, Mo, Cr, which immediately precede minima.)

Elements immediately following minima on ascending curves have low melting-points and relatively great volatility, such as the elements P, S, Cl, Ga, As, Se, Br, Sn, Sb, Te, I in successive sections of the curve. Here again it is noticed that the "typical" elements of low atomic weight are anomalous.

In general, increase in fusibility coincides with rise of atomic volume, and vice versa. Nevertheless the apices of the curves are occupied, not by the halogens or the inert gases, but by the less fusible alkali metals, which commence the periods.

*Other Physical Properties.*—Many other physical properties, so far as data permit, have been shown to vary periodically with atomic weight. Some of these will be briefly mentioned.

*Malleability.*—Only elements at or immediately following a maximum or minimum point are malleable; e.g.

Li, Be; Na, Mg at maxima,	
Fe, Co, Ni, Cu, Zn	} at minima.
Rh, Pd, Ag, Cd	

Brittle, heavy metals occur just before minimum points. Examples of these are—

V, Cr, Mn; Mo, Ru; Os, Ir.

The malleable metals are also the most ductile.

*Coefficient of Expansion.*—The researches of Fizeau tend to show that volatile elements on ascending curves have larger coefficients of expansion between  $0^{\circ}$  and  $100^{\circ}$  than difficultly fusible metals at minimum points.

*Atomic Refraction,* according to Gladstone, Landolt, and others, varies from a minimum at Group I to a maximum at Group IV.

*Colours of Salts.*—Bayley has pointed out that colourless acids only form coloured salts with metals at or near minimum atomic volume points, as may be readily perceived by reference to metals such as Mn, Fe, Co, Ni, Cu, Au, Pt.

*Conductivity for Heat and Electricity.*—Copper, silver, and gold, the best conductors, occur at transition points between difficultly and easily fusible metals. Thus:—

Fe	Co	Ni	Cu	Zn	Ga
Ru	Rh	Pd	Ag	Cd	In
Os	Ir	Pt	Au	Hg	Tl

Of similarly situated elements, those of higher are not generally such good conductors as those of lower atomic weight.

### CHEMICAL PROPERTIES

As a common criterion of the chemical characters of the elements, it may be well to employ their electro-chemical behaviour, as was done by Berzelius. Before, however, this can be done, it must be understood what is meant by the terms electro-positive and electro-negative, or, more simply, positive and negative, as applied to elements. It may be said that these terms are equivalent to the words metallic and non-metallic respectively. These latter expressions do not, however, convey any more definite meaning, when chemically considered, than the former ones.

Definite conceptions on this subject are derivable from the theory of electrolytic dissociation. Zinc and copper may be contrasted in their tendency to pass into the ionic state in solution. Since metallic zinc displaces hydrogen from dilute sulphuric acid, whilst copper is without action upon this acid,

zinc has a superior *solution pressure* to copper; and since cæsium reacts with water more vigorously than lithium, it, similarly, has a higher solution pressure than the latter element.

It is well known that this solution pressure of zinc expresses itself in the form of electro-motive force when solution of that metal takes place in a simple galvanic cell; and according to modern electro-chemical theories<sup>1</sup> the voltages which show the relative solution pressures of the metals are appropriately measured by the potential differences established between metals and their own salt solutions at standard dilution.

The following are a few of the values which have been thus observed:—

Mg in MgSO <sub>4</sub>	=	+1.24	volt
Zn „ ZnSO <sub>4</sub>	=	0.52	„
Cd „ CdSO <sub>4</sub>	=	0.16	„
Fe „ FeSO <sub>4</sub>	=	0.08	„
Cu „ CuSO <sub>4</sub>	=	−0.58	„
Ag „ Ag <sub>2</sub> SO <sub>4</sub>	=	−1.02	„

Whilst exact values have not been obtained in all cases, the following is the order of electro-potential of the principal metals:—

Cs, Rb, K, Na, Mg, Al, Mn, Zn, Cd, Tl, Fe, Co, Ni, Sn, Pb, H, Sb,  
Bi, As, Cu, Hg, Ag, Pd, Pt, Au.

This order represents also the relative power of displacing other metals from salt-solutions; so that any chosen metal can precipitate from solutions of equivalent strength any metals that follow it in the list.

The alkaline earth metals are not included in the list, but undoubtedly they should follow the metals of the alkalis.

The numerical values upon which the above series is based depend upon the tendency of the elements to pass into solution as basic ions. Thus the series illustrates what may be called the metallic reactivity of the metals, or their true electro-positiveness.

It is at once apparent, on consideration of this sequence, that

<sup>1</sup> For which works on electro-chemistry may be consulted.

*electro-positiveness* or metallic reactivity towards acids or salt solutions is not always the same thing as *chemical* positiveness or basic nature, as judged by the properties of oxides.

For example, whilst the alkali metals stand at the head of the list in both categories, arsenic and antimony, as shown by the properties of their oxides and other compounds, are less metallic—or more non-metallic—than copper or gold, although electrically they are more positive than these metals. Thus the electro-positive and base-producing properties of a metal are not always coextensive. Aluminium, for instance, is a powerfully electro-positive metal, but its basigenic properties are feeble. The term *basigenic* will be therefore employed when necessary to describe those characteristics of a metal which are expressed through the properties of its oxides and other compounds, and the term *oxygenic*<sup>1</sup> will similarly be used to denote the acid-producing property of a non-metal.

For the present, however, the agreement rather than the difference between the electrical and chemical properties of an element may be considered. Mention may be made of the following connected properties:—

(a) Power of mutual displacement and of combination under equivalent conditions.

(b) Relative thermal effect of combination.

(a) In a given combination of an element with a negative atom or group, a more electro-positive element will displace a less electro-positive. Thus, as before shown, zinc, which is more electro-positive than iron or copper, displaces these metals from solutions of their salts.

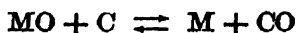
Similarly, in the higher oxyacids of the halogens, where those elements are united to negative oxygen, the more positive iodine will displace the less positive chlorine, *e.g.* from chlorates and perchlorates. And conversely, though in an entirely similar manner, the more negative chlorine displaces the less negative iodine from union with the positive atoms of the metals.

In general, combination will occur most readily between

<sup>1</sup> In its etymological sense.

elements most widely separated in electro-chemical character, though this statement must be taken with certain limitations. The actual result of a chemical reaction will depend on the conditions obtaining in the reacting system, and in a self-contained system may be shown to follow the law of mass action.

Thus, if chlorine and bromine were in competition for combination with a given amount of a metal, the actual amounts of chloride and bromide produced would depend on the relative active masses, that is, the number of equivalents per unit volume, of the competing elements, as well as upon their relative affinities; bromide might even preponderate in the product if bromine was originally present in considerable excess of chlorine, though a proper interpretation of the quantitative data would show that the affinity of the chlorine was superior. Again, many of the oxides of the metals are reduced by heating with the less positive carbon. Here it must be remembered that one of the products of reaction (oxide of carbon) is removed from the system as soon as it is formed, so that the reversible reaction



will proceed in the direction of the upper arrow to completion.

(b) Generally speaking, the thermal value of a reaction will be greatest when the uniting elements are most widely separated in chemical character. Thus the molecular heats of formation of the halogen acids are—

$$[\text{H}, \text{F}] = 389\text{K}, [\text{H}, \text{Cl}] = 220\text{K}, [\text{H}, \text{Br}] = 84\text{K}, [\text{H}, \text{I}] = -60\text{K}.$$

There is sometimes, as in the case of the alkali chlorides, not much difference in the heats of formation in a series. Laurie has shown that these heats of formation vary periodically.

Since combination is most likely to occur between elements widely separated in the chemical series, it appears that, of several possible reactions, that involving the greatest heat evolution may be expected to take place. This conclusion was expressed by Berthelot in his "law of maximum work"

or "the necessity of reactions", which asserted that "every chemical change accomplished without the addition of external energy tends to the formation of that body or system of bodies the production of which is accompanied by the development of the maximum quantity of heat". This statement is open to criticism because it denies that a reversible chemical reaction can occur, whilst it is well known that many reactions may be reversed by altering the conditions of concentration and temperature of the reacting substances.

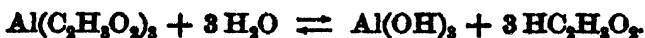
Thus endothermic reactions may take place at high temperature contrary to the provision of Berthelot's law, though at absolute zero only exothermic changes occur, and the law then becomes true.

When, however, the thermal value of a particular reaction is large, and the temperature not high, that reaction will probably take place, but great care must be exercised in interpreting the thermal data of a reaction, and definite knowledge of its conditions is necessary.

Finally, some general points connected with the electrochemical character of elements may be referred to.

The most electro-positive are the most typically metallic elements; their oxides are basic, and their hydroxides soluble in water and alkaline. They are the metals which produce true salts which are not decomposed by water and whose solutions are electrolytes.

Passing to the less electro-positive elements, oxides or hydroxides presenting a dual character are encountered, these being basic towards strong acids, and acidic towards strong bases. Of these, aluminium hydroxide,  $\text{Al}(\text{OH})_3$ , is a good example. Such oxides or hydroxides form salts which are more or less readily acted on by water yielding basic salts or even the hydroxides by *hydrolytic dissociation*; thus ferric chloride and the acetates of iron and aluminium are all hydrolysed.



With such metals, the character of the oxide is often deter-



mined by the proportion of oxygen present, that is, on the operative valency of the metal. Thus, while chromium forms the positive trivalent ion  $\text{Cr}^{+++}$ , hexavalent chromium appears as a constituent of the negative chromic acid ion  $\text{CrO}_4^{--}$ .

Finally, the electro-negative elements whose oxides are acidic yield acids as hydroxides. Their chlorides are not salts; they are in general distinguished by volatility; by the facts that they are not acted on by strong sulphuric acid, and that water decomposes them, yielding hydrochloric acid and the corresponding oxyacids of which they are the chloranhydrides.

The manner in which the chemical and electrical characteristics of the elements vary in the periodic classification may now be examined.

Starting from the alkali metals, the change in the first two periods is regular from basigenic and electro-positive to oxygenic and electro-negative. In the first period (Series 2) lithium is the most electro-positive, fluorine the most electro-negative element, beryllium is less electro-positive than lithium and more electro-positive than boron, and so on.

Similarly with the second period, sodium to chlorine. At the end of each period there is an abrupt change from negative to positive,—if the members of the helium group are ignored.

What is true for the first two short periods is also generally true for the succeeding long periods of seventeen elements; secondary periods are, however, discernible. A decrease in electro-positive character takes place from potassium through calcium and scandium to titanium and vanadium, which are somewhat electro-negative and oxygenic, their oxides yielding weak acids and their chlorides being volatile; chromium and manganese, and to a less extent iron, show a dual character, yielding both basic and acidic oxides; copper, though forming no acidic oxide, is less electro-positive than zinc, whose hydroxide nevertheless dissolves in alkalis. From gallium electro-negative and oxygenic characters increase through germanium, arsenic, and selenium to bromine. The

elements of the next long period, from rubidium to iodine, show similar relationships.

It is to be noted that the members of the B sub-group are always less electro-positive than the corresponding members of the A sub-group. Thus zinc is less electro-positive than calcium, arsenic than vanadium, bromine than manganese.

The variation in character from member to member of a group is perhaps one of the most valuable regularities revealed by the periodic classification, affording, as it does, the key to the systematics of a group. This variation is from less to more electro-positive, with increase of atomic weight in every group and sub-group with three exceptions, these being the eighth group, and sub-groups IB and IIB. Thus in Group IA of the alkali metals, lithium is the least and caesium the most electro-positive; and in Group VII B of the halogens, fluorine is the least and iodine the most electro-positive, or fluorine the most and iodine the least electro-negative.

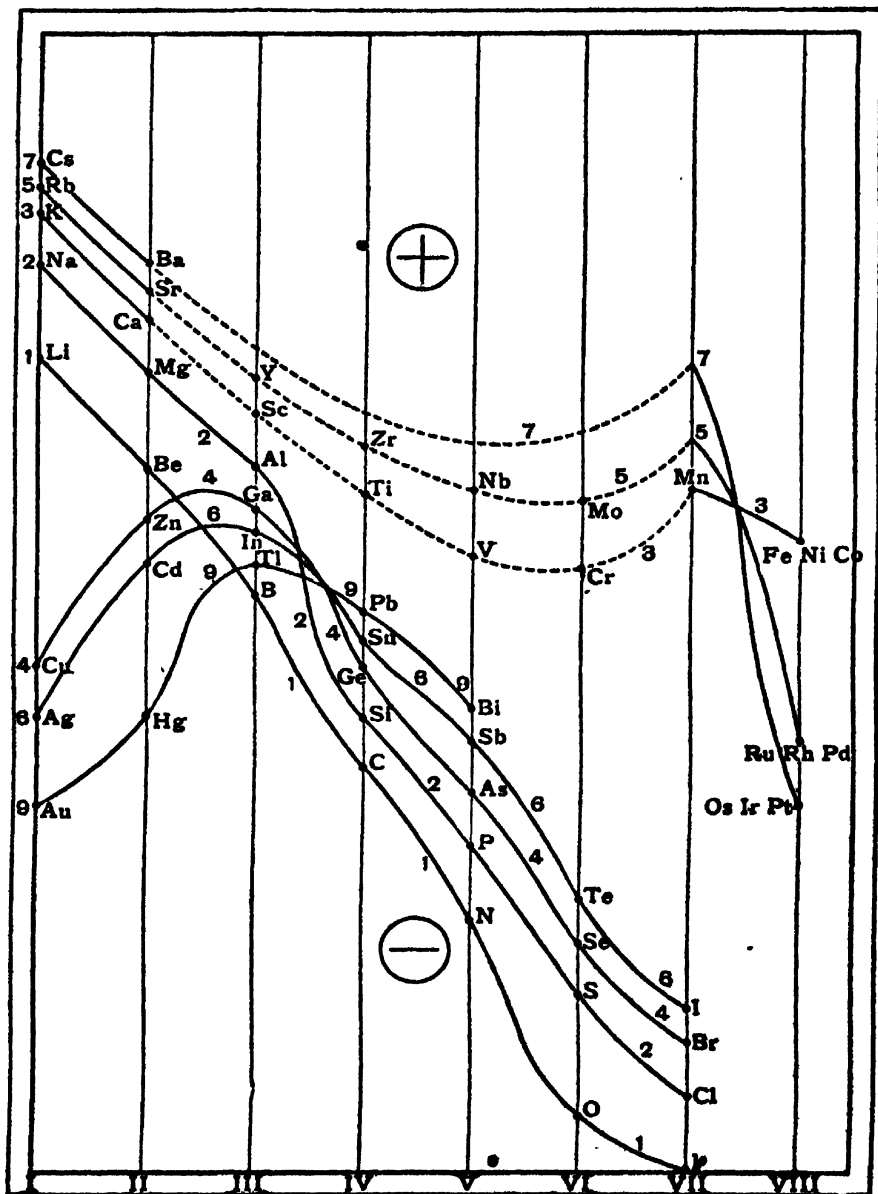
The exceptional relationships of the elements of the eighth group and the sub-groups IB and IIB are connected with the feeble reactivity of these elements and the corresponding ease with which they are separated from their compounds. And since this reactivity diminishes with increase in atomic weight so that the elements osmium, iridium, platinum, gold, and mercury are the most easily reducible of the metals, it follows that these metals are also among the most electro-negative; for, as before observed, metallic electro-negativeness, as indicated by position in the electro-potential series, is identical with metallic inertness. If gold is accepted as the most electro-negative metal, sub-group IB being the sub-group in which metallic inertness is most highly developed, the relative positions of the six metals

Cu, Hg, Ag, Pd, Pt, Au

in the electro-potential series are not inconsistent with their positions in the periodic table.

The diagram on the opposite page, constructed by Abegg,<sup>1</sup>

<sup>1</sup> *Zett. Anorg. Chem.* xxxix. 367.



Gradation of Electro-Potential in the Periodic System. (After E. Abegg.)

Copied by permission from *Zeit. Anorg. Chem.*, xxxix. 387.

shows approximately the periodic variation of electro-positiveness with atomic weight. The exceptional relationships of the elements of the eighth group are shown on the right after the intersection of the three upper curves, and those of the elements of groups IB, IIB, and possibly IIIB by the three ascending curves on the left, which, it will be observed, intersect before the fourth group is reached.

Thus there is in the periodic chart a region comprising group VIII and sub-groups IB and IIB, where chemical inertness and corresponding electro-negativeness are the chief characteristics, and that these characteristics increase with rising atomic weight in these groups. When the chart is on a cylinder this region is diametrically opposite to that occupied by the no-valency elements of the helium group.

The relationship of electro-positiveness to basigenic properties within these groups must however be discussed. It is within this region that the two properties appear not to be coextensive. Probably iron, cobalt, and nickel are more basigenic than the following elements of the eighth group, as they are more electro-positive; but whilst silver is more electro-negative than copper, it is nevertheless also more basigenic, since its oxide shows a faintly alkaline reaction with water, and its salts, in contradistinction to the cuprous salts, are stable towards water. But cadmium, although less electro-positive, is more basigenic than zinc, since its hydroxide is not dissolved by alkalis,<sup>1</sup> and its salts are not so easily hydrolysed as those of zinc.

It may further be observed that in all other groups but those just considered, the increase of basigenic—or electro-positive—properties is directly connected, as far as this is possible, with the loss of acid-producing, that is, oxygenic, properties, this being particularly noticeable in the fifth group.

In these exceptional sub-groups, however, there is no appreciable development of oxygenic with electro-negative properties; so that gold, the most electro-negative metal, does not form

<sup>1</sup> It may be that  $\text{Zn}(\text{OH})_2$  does not form a true compound with  $\text{NaOH}$ , but that alkali merely causes the  $\text{Zn}(\text{OH})_2$  to assume the colloidal state, and thereby aids the solution of zinc by water.

stable acids, whilst arsenic, which is far less electro-negative, is far more oxygenic, forming well-defined acids. Possibly a conflict between these two tendencies—the tendency towards chemical inertness with electro-negativeness, and the tendency towards oxygenic properties also combined with electro-negativeness—may account for the anomalies noticed in these exceptional sub-groups, as, for example, in the case of cadmium and zinc.

From what has been said, it will now be seen that the diagonal drawn from lithium in the tabular arrangement, Group VIII being excluded, approximately divides the elements in such a way that those in the lower section are the more electro-positive or basigenic, and those in the upper section the more electro-negative or oxygenic, in character; this being connected with the fact previously observed that the elements of the B or odd sub-groups are more electro-negative than their congeners in the A or even sub-groups.

*Valency.*—The maximum valency as shown in hydrogen, chlorine, and oxygen compounds varies periodically.

*Hydrogen Valency.*—The members of sub-groups A, being the more metallic elements, do not form gaseous hydrides.<sup>1</sup> Among gaseous hydrides of boron,  $\text{BH}_3$  is almost certainly to be included, and definite hydrides appear in Group IV ( $\text{CH}_4$  and  $\text{SiH}_4$ ). In Group V there are  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{AsH}_3$ ,  $\text{SbH}_3$ ; in Group VI,  $\text{OH}_2$ ,  $\text{SH}_2$ ,  $\text{SeH}_2$ ,  $\text{TeH}_2$ ; and in Group VII,  $\text{FH}$ ,  $\text{ClH}$ ,  $\text{BrH}$ ,  $\text{IH}$ .

Thus the hydrogen valency in the various groups is as follows:

Group	III	IV	V	VI	VII
	3	4	3	2	1;

clearly showing the periodic dependence of this property on atomic weight.

The stability of the hydrides increases from IV to VII. This is not well shown by the hydrides of the non-metallic

<sup>1</sup> Solid hydrides of definite composition are formed by the union of hydrogen with certain metals; e.g.  $\text{NaH}$ ,  $\text{KH}$ ,  $(\text{CuH})_x$ ,  $\text{CaH}_2$ ,  $\text{BaH}_2$ . Palladium absorbs hydrogen, but no definite compound is formed.

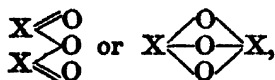
elements of Series 2, but is evident from a comparison of those of Series 3,  $\text{SiH}_4$ ,  $\text{PH}_3$ ,  $\text{SH}_2$ ,  $\text{ClH}$ . This is in accordance with the development of non-metallic properties in passing along the series. In this connection it may be remarked that it is only the relatively non-metallic elements of the odd series, or the B sub-groups, in the long periods which form stable, volatile, alkyl compounds.

*Chlorine Valency.*—The highest chlorine compounds of the respective groups are represented by the following types:—

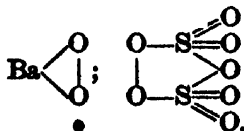
Group	I	II	III	IV	V	VI	VII	VIII
Type	$\text{XCl}$	$\text{XCl}_2$	$\text{XCl}_3$	$\text{XCl}_4$	$\text{XCl}_5$	$\text{XCl}_6$	—	$\text{XCl}_4$

In Group V the form  $\text{XCl}_5$  and not  $\text{XCl}_3$  is the more stable; in Group VI the form  $\text{XCl}_6$  is represented only by  $\text{WCl}_6$ , the type  $\text{XCl}_4$  being more typical; in Group VIII the tetrachloride is the highest form, and in Group I the type  $\text{XCl}$  is departed from in  $\text{CuCl}_2$  and  $\text{AuCl}_3$ . A periodicity is nevertheless perceptible.

*Oxygen Valency.*—The term “oxygen valency” refers to that valency displayed in the highest typical oxide, by which must be understood the highest oxide in which each oxygen atom is united only to the nuclear atom or atoms of the second element; as, for example, in the Group III oxides  $\text{X}_2\text{O}_3$ ,



as distinguished from the peroxides of higher oxygen content, in which linkages of oxygen atoms to one another is found, as in  $\text{BaO}_2$  and  $\text{S}_2\text{O}_7$ .



The following oxides, taken in the order of the groups, are typical:—



Thus oxygen valency rises continuously from 1 to 8,

Group	I	II	III	IV	V	VI	VII	VIII
O. Valency	1	2	3	4	5	6	7	8,

though from phosphorus onwards lower oxygen valencies likewise appear.

The degree of hydroxylation of which these oxides are capable is instructive.

Sodium and magnesium oxides form the hydroxides  $\text{NaOH}$  and  $\text{Mg(OH)}_2$ ; the latter, however, is less stable than  $\text{NaOH}$ , being decomposed at a low red heat, and not being formed by direct combination of the oxide with water.  $\text{Al(OH)}_3$  is more unstable than  $\text{Mg(OH)}_2$ , and loses water on exposure to the air; the aluminates, too, are chiefly meta-salts.  $\text{Si(OH)}_4$  probably exists in dilute solution, and certain ortho-silicates corresponding to it are known; on decomposition it easily yields  $\text{SiO(OH)}_2$  and  $(\text{SiO}_2)_n$ .  $\text{P(OH)}_5$  is unknown, and the first anhydride,  $\text{PO(OH)}_3$ , easily loses water, forming  $\text{P}_2\text{O}_3(\text{OH})_4$  and  $\text{PO}_2\text{OH}$ , the latter of which, however, is stable at a red heat.  $\text{S(OH)}_6$  and  $\text{SO(OH)}_4$  are both unknown, and the meta-acid  $\text{SO}_2(\text{OH})_2$  is easily broken up into  $\text{SO}_3$  and water.

Salts corresponding to  $\text{IO(OH)}_5$  are known, but the halogen oxyacids derived from  $\text{X}_2\text{O}_6$  are monobasic, corresponding to  $\text{XO}_2\text{OH}$ .

Lastly,  $\text{OsO}_4$  is incapable of hydroxylation, its solution in water being neutral in reaction.

It will be observed that a gradation is manifested by these oxides as regards power of combining with water, and that, except for those remarkable salts, the periodates, the power of hydroxylation reaches a maximum with  $\text{Si(OH)}_4$ , and diminishes, like power of combining with hydrogen, through the fifth, sixth, and seventh groups to the eighth group.

## ✓ PRACTICAL APPLICATIONS OF THE PERIODIC LAW

To be a valid natural law the periodic law must operate as an instrument both of control of present knowledge and of

discovery of new facts. From such successful applications this law derives its most valuable support.

It has been practically applied in two main directions: firstly to the correction of atomic weight values, and secondly to the description of the properties of unknown elements. Atomic weight corrections, instigated by the law, have been of two kinds: (a) small corrections affecting the position of an element in series, and (b) the determination of the correct multiple of the combining weight of an element, when this is otherwise doubtful. To case (a) may be referred the correction of the atomic weight of caesium determined by Bunsen as 123.4. If this value is accepted, the difference  $\text{Cs} - \text{Rb} = 37.95$ , whereas in greater likelihood it should equal  $\text{Rb} - \text{K} = 45.35$ . Redetermination with larger quantities of material gave  $\text{Cs} = 132.81$  and  $\text{Cs} - \text{Rb} = 47.36$ , which is in accordance with the law.

The second application (b) of the law to atomic weight determination may be illustrated by the cases of indium, beryllium, and uranium. The chemical equivalent of indium is  $38.27^1$ . If the oxide be  $\text{InO}$ , as was formerly thought, the atomic weight is 76.54. This value places the metal between arsenic and selenium, a position inconsistent with its chemical properties. If, however, the oxide be  $\text{In}_2\text{O}_3$ , the atomic weight becomes 114.8, and the element is placed between cadmium and tin in Group III, along with the analogous metal thallium. This change, suggested by Lothar Meyer, was warranted by Bunsen's determination of the specific heat as 0.057, whence

$$\text{In} = \frac{6.4}{0.057} = 112.3.$$

The equivalent weight of beryllium is 4.55. From the isomorphism of the oxide and sulphate with the corresponding aluminium compounds, Nilson and Petterson attributed the atomic weight 13.65 to this element, the oxide being  $\text{Be}_3\text{O}_5$ ; and this value was confirmed by their determination of the specific heat as 0.4079. Beryllium thus falls into an extremely unlikely position between carbon and nitrogen. In



spite of the above facts, Mendeléeff considered 9 the correct value for the atomic weight, and placed the metal in Group II. Brauner suggested that the specific heat might vary with temperature, and Humpidge found that between  $400^{\circ}$  and  $500^{\circ}$  this value becomes constant and equal to 0.62, thus giving an atomic weight approximating to 9. Moreover, Carnelley pointed out that the melting-point of the chloride, about  $600^{\circ}$ , does not agree well with the formula  $\text{BeCl}_2$ , the analogously constituted chlorides  $\text{BCl}_3$  and  $\text{AlCl}_3$  possessing far lower melting-points. Finally Nilson and Petterson succeeded in vaporizing the chloride and ascertaining its molecular weight, whence  $\text{Be} = 9.1$ , a value agreeing with the periodic law.

The atomic weight formerly assigned to uranium was approximately either 60 or 120. Mendeléeff showed that these values did not place uranium in a probable position in the classification, and preferred the value 240, regarding uranium as the heaviest analogue of chromium, the highest oxide being acidic, but less strongly so than chromic anhydride, and forming uranates analogous to the chromates. Further, the highest chloride resembles  $\text{MoCl}_4$  in volatility. Determinations of the vapour densities of the chloride and bromide by Zimmermann confirmed Mendeléeff's value.

The second application of the periodic law, to the description of the properties of hitherto unknown elements, affords perhaps the best test of the value of the law. The possibility of such a prediction depends upon the principle that the properties of an element are the mean of those of its atomic analogues. The atomic analogues are those elements immediately preceding and succeeding an element in series and group. Thus the analogues of phosphorus are silicon and sulphur in series, and nitrogen and arsenic in group. The atomic weight, 31.04, is nearly the mean of those of silicon and sulphur. The hydrogen valency is three, that of silicon being four, and of sulphur two. Phosphorus is intermediate in chemical respects between nitrogen and arsenic. It is more positive than nitrogen and less so than

arsenic; hence its hydride is but feebly basic, its pentoxide is acidic but less so than that of nitrogen, its chlorides are more stable than nitrogen chloride but are more readily decomposed by water than arsenic chloride.

When Mendeléeff first put forward the periodic classification he sketched the properties of three elements, which if discovered would fill blank spaces then existing in the table. These elements, now known as gallium, scandium, and germanium, he named respectively <sup>1</sup>eka-aluminium, eka-boron, and eka-silicon, from their analogy with these three known elements. A comparison of the predicted with the actual properties of these elements is interesting.

Eka-aluminium, following zinc in series, and placed between aluminium and indium in group, would be a metal of atomic weight = 69, of low melting-point, and density = 5.9. It would not readily be acted on by air, and would dissolve in acids and alkalis. It would form a potassium alum, and its oxide and chloride would be  $\text{Ea}_2\text{O}_3$  and  $\text{Ea}_2\text{Cl}_6$  respectively. Gallium, discovered in 1875 by de Boisbaudran, has an atomic weight of 69.9, fuses at  $30.15^\circ$ , and has a density of 5.93. It is not volatile, and is only superficially oxidized in air at a red heat. It decomposes water at high temperatures, and is soluble in hot hydrochloric acid and potassium hydroxide. It forms well-defined alums, and its oxide and chloride are  $\text{Ga}_2\text{O}_3$  and  $\text{Ga}_2\text{Cl}_6$  or  $\text{GaCl}_3$ .

Eka-boron would be related to aluminium in the same way as calcium is to magnesium. Its atomic weight would lie between 43 and 46. The oxide  $\text{Eb}_2\text{O}_3$ , density 3.5, would be soluble in acids, but, being more basic than  $\text{Al}_2\text{O}_3$ , would not be soluble in caustic alkalis. Its salts would be colourless and give gelatinous precipitates with alkalis, alkali carbonates, and phosphates. The sulphate would form double salts, probably not isomorphous with the alums. The chloride would be less volatile than  $\text{AlCl}_3$ .

The properties of scandium, discovered by Nilson, fully correspond. The element has the atomic weight 44.1. Its

<sup>1</sup> The prefix eka = one in Sanskrit.

oxide  $\text{Sc}_2\text{O}_3$ , of density 3.8, is soluble in strong acids, but not in alkalis. Solutions of the salts give gelatinous precipitates with sodium hydroxide, carbonate, and phosphate. The sulphate forms a double salt  $3\text{K}_2\text{SO}_4, \text{Sc}_2(\text{SO}_4)_3$  which is not an alum. The chloride  $\text{ScCl}_3$  breaks up when heated in the air, producing a basic chloride and  $\text{HCl}$ .

Eka-silicon, lying between silicon and tin, would be related to titanium as zinc is to calcium. Its atomic weight would be about 70. It would be a gray, difficultly fusible metal, obtained by reduction of the oxide with sodium or carbon, and would be scarcely acted on by acids, but readily by alkalis. The oxide  $\text{EsO}_2$  would be less basic than titanium dioxide and more so than silicon dioxide. The fluoride would not be gaseous, and would give rise to double fluorides  $\text{M}_2\text{EsF}_6$ , isomorphous with silicifluorides. The chloride would be a liquid boiling at about  $100^\circ$ . The properties of germanium, discovered by Winkler, fully confirm those predicted. The atomic weight is 72.5, and the metal is obtained by reduction of the oxide by carbon or hydrogen; germanifluorides isomorphous with silicifluorides may be obtained. The chloride  $\text{GeCl}_4$  is a liquid, boiling at  $86^\circ$ .

These facts sufficiently vindicate the periodic law as an instrument of discovery. In astronomy the discovery of new planets, whose existence has previously been foretold by mathematical calculations, has always been considered as a powerful proof of the correctness of the theories on which such calculations are based. A similar conclusion may be drawn in the case of the periodic law.

### OBJECTIONS TO THE PERIODIC CLASSIFICATION

The most recent determinations of the atomic weight of tellurium confirm the position of that element as following and not preceding iodine in series. The atomic weight of argon, as will be seen subsequently, places that element between potassium and calcium. It can hardly be expected that any future determinations of the atomic weights of these two elements will alter their values sufficiently to allow them to

be placed in the positions in the periodic classification which their properties demand, and this consideration really constitutes a serious objection to the periodic law. It may, however, be pointed out that nowhere do atomic weight differences present strict mathematical relationships, though only in these two cases is the variation sufficiently great to disturb the order of atomic weights.

A further objection is that the arrangement of the elements according to their atomic weights is sometimes in opposition to that which would be made in a classification according to properties. Thus the sub-group copper, silver, gold displays scarcely any likeness to that of the alkali metals; and even when, as in the case of silver, the type of compounds formed is similar, there is wide divergence in the properties both of the metals and their compounds. For example,  $\text{Ag}_2\text{O}$  and  $\text{Li}_2\text{O}$ ,  $\text{AgCl}$  and  $\text{NaCl}$ , differ greatly in properties. It is, however, in Groups I and VII that the provisions of the periodic law would suggest the greatest dissimilarity between the sub-groups. Copper, silver, and gold approximate in properties to their neighbours in the eighth group, nickel, palladium, and platinum, so that sometimes they have been considered to belong properly to this group. The absence of uniformity of type in the group is, however, anomalous. The trivalency of gold, which appears most unaccountable, enables this element, however, to form one of the following series of chlorides:—



Divalent iron and manganese in many respects resemble in their compounds the metals of Group II, especially magnesium. Trivalent iron, manganese, and chromium similarly resemble aluminium and the Group III metals. Hexavalent manganese and iron are allied, in manganates and ferrates, to the sulphur group. Manifestly, it would not be permissible to place an element like iron in more than one group. The difficulty may, however, in great measure be overcome in view of the circumstance that the group type is usually best revealed in the compounds of highest valency; thus in Group VII the per-

manganates ally manganese with the halogens. When, as in the metals named, an element displays several valencies, it is to be expected that the properties of the compounds of types corresponding to these valencies will be similar to those of other compounds of the same type.

In several cases the periodic classification separates into different groups elements which show chemical similarities; and this objection has some weight. As examples, Cu and Hg, Ba and Pb, Ag and Tl may be given. Relationships between these three pairs of metals is shown by reason of isomorphism and solubility of certain salts; but it is open to question whether their differences are not greater than their resemblances. The metals copper and mercury show great contrast in physical properties; copper has a high melting-point, while mercury forms the last of a sub-group of metals whose melting and boiling points fall with rising atomic weight. Cupric chloride and mercuric chloride, cupric sulphate and mercuric sulphate resemble one another but slightly, as a consideration of their behaviour towards water will show. Even the resemblance between cuprous and mercurous chlorides is not so great as at first sight appears, and cuprous and mercurous oxides and sulphates differ very widely in stability. Similarly with lead and barium:  $\text{PbO}_2$ , the typical oxide of lead, is in no way analogous to  $\text{BaO}_2$ , and even  $\text{PbO}$  shows slight acidic properties in utter contrast to  $\text{BaO}$ ; also the metals themselves differ widely. With reference to silver and thallium, the oxide  $\text{Tl}_2\text{O}_3$ , although unstable, bears out the properties of the group type, and it is not surprising that the oxide and chloride  $\text{Tl}_2\text{O}$  and  $\text{TlCl}$  resemble other compounds of the same type. The chemical relationship of thallium to the alkali metals and to lead is, however, quite as great as to silver.

The placing of the elements of the rare earths in the existing periodic classification is also difficult. Werner<sup>1</sup> has, however, lately suggested that the long period beginning with caesium may actually contain a larger number than 18 elements, and that the rare earth metals thus lie between barium and tanta-

<sup>1</sup> Ber. 1906, xxxvii. 914.

lum in that long period, which he supposes to contain 33 elements. Just as there is an increase in the number of elements in passing from the two short to the two long periods, so, according to Werner, there is also an increase in passing from the long periods to the incomplete periods commencing with cæsium and its unknown higher homologue. As will be seen under Group III, the atomic volumes of these elements cause them to be placed upon a descending portion of the curve between barium and tantalum.

#### POSITION OF THE INERT GASES OF THE HELIUM GROUP

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The gases of the helium group, viz. helium, ~~3.99~~<sup>3.99</sup>; neon, ~~32.02~~<sup>32.02</sup>; argon, ~~39.8~~<sup>39.8</sup>; krypton, ~~83.7~~<sup>83.7</sup>; xenon, ~~130.2~~<sup>130.2</sup>, are all monatomic, elementary substances, devoid of chemical activity. They therefore constitute the group of no-valency elements, and it is necessary to assign them a position in the periodic classification. At the time of their discovery it was thought by some that these gases could find no place in the periodic scheme, especially as argon could not be placed between potassium and calcium, as its atomic weight demanded.

On the other hand, even previous to the discovery of the new elements, it was suggested by Flawitsky and Thomsen that a group of elements probably exists whose electro-chemical characters are  $\pm \infty$ , and whose valency is 8 or 0. If the elements are arranged according to the periodic system, but on a cylindrical instead of on a plane surface, H and Li, F and Na, Cl and K, Br and Rb, I and Cs are respectively adjacent, the transition in each case being from an extremely electro-negative to an extremely electro-positive element. Now in the long periods the members of the eighth group serve as neutral transitional elements between Groups VII A and I B; and whilst they manifest a maximum valency of eight, their occurrence in the free state in nature, the resistance which they offer to combination, and the inertness of their compounds suggest at least some analogy to the properties of the no-

valency elements of the helium group. It is not an unreasonable suggestion, therefore, that these latter elements should be interposed between the pairs of elements given above, to modify the extreme transition from non-metallic to metallic characteristics.

(Thus the change from extremely electro-negative to extremely electro-positive properties will be made in each case through an element which is chemically indifferent, and has no valency.) According to Thomsen, the existence of such a group of elements may perhaps be thus explained: "that on account of a particular simple and enclosed arrangement of the constituent atoms, a molecule may be formed which offers no points of attack, consequently can form no stable compounds, and only obeys the universal law of gravitation".

It is true that the law of octaves is destroyed by the interpolation of the elements of the helium group, but it will be seen from the following scheme that these five elements are thus suitably placed in the periodic table:—

H	He	Li
1·008	3·99	6·94
F	Ne	Na
19·0	20·2	23·00
Cl	A	K
35·46	39·88	39·10
Br	Kr	Rb
79·92	82·9	85·45
I	Xe	Cs
126·92	130·2	132·81

Further support is given to this conclusion by data concerning the atomic volumes of argon, krypton, and xenon, which, in the liquid state, are approximately equal to 35. In accordance therewith, these elements find places on Lothar Meyer's curve of atomic volumes without changing the character of that curve; and thus they take a permanent place in the periodic system.

## CHAPTER III

## OXIDES, HYDROXIDES, AND ALLIED COMPOUNDS

Oxides, or binary compounds of oxygen and other elements, are known in the case of every element except fluorine and bromine; the existence of hypobromous and bromic acids, however, warrants the assumption that the anhydrides  $\text{Br}_2\text{O}$  and  $\text{Br}_2\text{O}_5$  are at least capable of existence.

On account of their universality, and of their simple relationships to the basic and acidic hydroxides, a study of the characteristics of the oxides of a group is of great value for comparative purposes.

In the periodic classification, the typical oxide of the group is the highest oxide which displays basic or acidic character; for example, in Group II the oxides  $\text{MO}$ , corresponding to the salts  $\text{MX}_2$ , in Group VI the oxides  $\text{MO}_3$ , corresponding to the acids  $\text{H}_2\text{MO}_4$ , are the typical oxides. Higher oxides, such as  $\text{MO}_2$  in Group II, and  $\text{M}_2\text{O}_7$  in Group VI, are peroxides.

Oxides are classified in four main groups: *basic*, *acidic*, *neutral*, and *peroxides*.

*Basic oxides* differ in character according to the degree of electro-positiveness of the metal from which they are derived. The oxides of the most electro-positive elements, such as the alkali metals, are very stable, whilst those of the electro-negative metals, according to the electro-potential series, such as mercury, silver, and gold, are unstable, being easily decomposed by heat into metal and oxygen. The more strictly chemical differences, whose significance from the point of view of classification is greater, are shown in the manner of formation and properties of the hydroxides, as will appear later.

*Acidic oxides* are formed by non-metallic elements, and their hydroxides are the oxyacids.

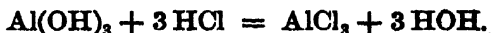
It must, however, be clearly understood that the terms basic and acidic are strictly relative. A large class of oxides and



hydroxides exhibit both properties. These are the oxides of elements of ill-defined chemical property, which occur at transition points between basigenic and oxygenic elements in a series or group. (As examples may be quoted the hydroxides of zinc and aluminium,<sup>1</sup> which are soluble in caustic alkalis, and towards which they behave as acids; thus:—



Towards strong acids, however, they behave as bases; thus:—



Such salts as the zincates and aluminates of sodium and potassium are naturally characterized by great instability, being decomposed by weak acids, even by carbonic acid, and in some instances, as in that of sodium chromite,  $\text{Cr(ONa)}_3$ , even by boiling the aqueous solution.)

*Neutral oxides* are such as form neither basic nor acidio hydroxides, nor yield such oxides by loss of oxygen. Water, carbon monoxide, nitrous and nitric oxides, are examples of such compounds. (Carbon monoxide and nitrous oxide, however, are formed from formic and hyponitrous acids respectively, by loss of water,) so that, although they do not unite with water to form these acids, their relation to them is such that they cannot be considered neutral oxides in the narrower sense.

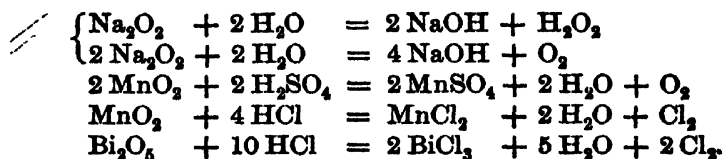
Suboxides, such as  $\text{Ag}_2\text{O}$  and  $\text{Pb}_2\text{O}$ , may, however, be said to belong to this class, as well as the tetroxides  $\text{RuO}_4$  and  $\text{OsO}_4$ , which are peculiar in not combining with water or alkalis. The latter oxides are also, in fact, both basic and acidic peroxides, since compounds in which the metal performs either acidic or basic functions are obtainable from these oxides by reduction.

A *peroxide*, in the stricter sense, is an oxide containing more oxygen united to a certain quantity of an element than is

<sup>1</sup> It may be observed that, although feebly basigenic, zinc and aluminium are powerfully electro-positive metals. The difference between these two properties has already been referred to in Chapter II.

contained in its highest typical oxide according to the periodic law. There are, therefore, *basic* and *acidic peroxides*. In this definition no account is taken of the various reactions in which an oxide may participate. For instance, manganese and lead dioxides, as well as bismuth pentoxide, are not peroxides in the sense of the definition, because their oxygen content does not exceed that of the typical oxides, which are  $\text{Mn}_2\text{O}_7$ ,  $\text{PbO}_2$ , and  $\text{Bi}_2\text{O}_5$  respectively.  $\text{Na}_2\text{O}_2$ ,  $\text{K}_2\text{O}_4$ ,  $\text{BaO}_2$ ,  $\text{S}_2\text{O}_7$  are, however, true peroxides. When, however, the first-mentioned oxides are attacked by acids, they form salts of the oxides  $\text{MnO}$ ,  $\text{PbO}$ , and  $\text{Bi}_2\text{O}_3$  respectively. Hence higher oxides than these and other salt-forming oxides are often considered to be basic peroxides.

Some typical reactions of basic peroxides are here set forth:—

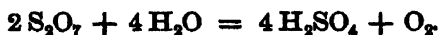


The reaction with hydrochloric acid is highly characteristic of peroxides, the amount of chlorine evolved being equivalent to the oxygen present in the peroxide in excess of that in the basic oxide corresponding to the salt formed. It may sometimes be assumed that a perchloride is first formed equivalent to the peroxide, and that this subsequently evolves chlorine. Such an assumption is only admissible when the higher chloride is known to exist.

Another very general reaction of peroxides is the formation by them of salts corresponding to true basic oxides by direct union with lower acidic oxides. Sodium dioxide, when gently warmed in sulphur dioxide, burns, producing sulphate:  $\text{Na}_2\text{O}_2 + \text{SO}_2 = \text{Na}_2\text{SO}_4$ , and lead dioxide behaves similarly:  $\text{PbO}_2 + \text{SO}_2 = \text{PbSO}_4$ . In these reactions the peroxides behave as oxidizing agents. Such a property, however, is not in itself sufficient to justify the designation peroxide, for

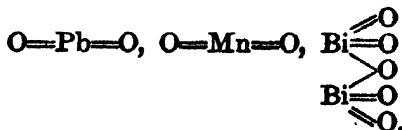
certain unstable oxides, such as  $\text{Ag}_2\text{O}$ , are oxidizing agents, though not peroxides.

The properties of acidic peroxides are at first sight more complex, but are only apparently so. A true acidic peroxide is one, like the anhydride of perchromic or persulphuric acid, containing a higher oxygen content than the highest typical oxide of the group, so that by loss of oxygen in presence of water a typical acid is formed. Thus persulphuric anhydride readily decomposes with water in the following way:-

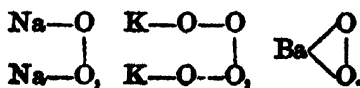


Permanganic anhydride,  $\text{Mn}_2\text{O}_7$ , also yields a lower oxide, and oxygen, though not so readily as  $\text{S}_2\text{O}_7$ . It is not, however, a true acidic peroxide, because it is a typical oxide of the seventh group, and possesses normal properties as an acidic oxide; also, as will be seen later, its constitution differs essentially from that of  $\text{S}_2\text{O}_7$ . As indicated above, it might be considered to be a basic peroxide.

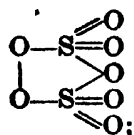
Mendeléeff has suggested a manner of classification of peroxides on structural grounds, depending on the valency of the element united to oxygen. The oxygen atom or atoms, over and above those required to form the basic oxide, may either be doubly linked to the metal atom, or singly linked to the metal and to oxygen, forming a chain, and so preserving the valency of the metal in the basic oxide unchanged. The dioxides of lead and manganese, and bismuth pentoxide, represent the first type, and are called *polyoxides*; thus:—



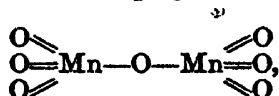
The peroxides of the metals of Groups I A and II A and B conform to the second type, and are called *superoxides*. They are thus formulated:—



Mendeléeff represents sulphur heptoxide, also, as a superoxide—



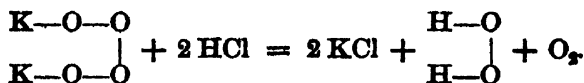
but manganese heptoxide is a polyoxide, thus:—



since it does not contain an oxygen chain.

It will be observed that the true basic and acidic peroxides are superoxides, whilst those normal acidic oxides which behave as oxidizing agents are polyoxides.

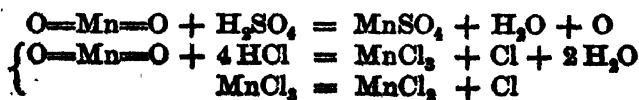
A mode of distinguishing between the two classes is to be found in their behaviour towards an excess of water or dilute acid. A superoxide containing the group  $\begin{array}{c} \text{—O} \\ | \\ \text{—O—} \end{array}$  yields hydrogen peroxide as a characteristic product, thus:—



A polyoxide, however, like lead or manganese dioxide, is usually not attacked by dilute acids; with strong sulphuric or hydrochloric acid oxygen or chlorine is evolved, though of course the same is true of the action of a strong acid on a superoxide.

The mechanism of the evolution of oxygen or chlorine is, however, probably different in the two cases.

With a polyoxide, *e.g.*  $\text{Mn}_2\text{O}_7$ , and strong  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$ , the following reactions take place:—



## CLASSIFICATION

Group.	Basic.	Basic and Acidic.	Acidic.
I.	{ Li <sub>2</sub> O, Na <sub>2</sub> O, K <sub>2</sub> O, Rb <sub>2</sub> O, Cs <sub>2</sub> O }		
B.	Cu <sub>2</sub> O, CuO, Ag <sub>2</sub> O, (AgO), Au <sub>2</sub> O		
II.	{ CaO, SrO, BaO, MgO, CdO, Hg <sub>2</sub> O, HgO }	BeO, ZnO	
III.	{ Sc <sub>2</sub> O <sub>3</sub> , Y <sub>2</sub> O <sub>3</sub> , La <sub>2</sub> O <sub>3</sub> , Ti <sub>2</sub> O <sub>3</sub> , Ti <sub>2</sub> O <sub>5</sub> }	Al <sub>2</sub> O <sub>3</sub> , Ga <sub>2</sub> O <sub>3</sub> , In <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>
A.	{ Ti <sub>2</sub> O <sub>3</sub> , Ti <sub>2</sub> O <sub>5</sub> , ZrO <sub>2</sub> , Ce <sub>2</sub> O <sub>3</sub> , CeO <sub>2</sub> , ThO <sub>2</sub> }	TiO <sub>2</sub>	
IV.			{ (CO), CO <sub>2</sub> , SiO <sub>2</sub> , GeO <sub>2</sub> , SnO <sub>2</sub> , PbO <sub>2</sub> }
B.		GeO, SnO, PbO	
V.	A. V <sub>2</sub> O <sub>3</sub> , V <sub>2</sub> O <sub>5</sub>	V <sub>2</sub> O <sub>4</sub> , V <sub>2</sub> O <sub>5</sub>	Nb <sub>2</sub> O <sub>5</sub> , Ta <sub>2</sub> O <sub>5</sub>
B.	Bi <sub>2</sub> O <sub>3</sub>	Sb <sub>2</sub> O <sub>3</sub>	{ (N <sub>2</sub> O), N <sub>2</sub> O <sub>3</sub> , NO <sub>2</sub> *, N <sub>2</sub> O <sub>5</sub> , P <sub>4</sub> O <sub>6</sub> , P <sub>2</sub> O <sub>5</sub> *, P <sub>4</sub> O <sub>10</sub> , As <sub>2</sub> O <sub>3</sub> , Sb <sub>2</sub> O <sub>3</sub> , (Bi <sub>2</sub> O <sub>3</sub> ) }
VI.	A. { CrO, MoO, Mo <sub>2</sub> O <sub>3</sub> , (WO <sub>2</sub> ), UO <sub>2</sub> }	Cr <sub>2</sub> O <sub>3</sub> , MoO <sub>3</sub> , UO <sub>3</sub>	CrO <sub>3</sub> , MoO <sub>3</sub> , WO <sub>3</sub>
B.			{ S <sub>2</sub> O <sub>3</sub> (?), SO <sub>2</sub> , SO <sub>3</sub> , SeO <sub>2</sub> , TeO <sub>2</sub> , TeO <sub>3</sub> }
VII.	A. MnO, Mn <sub>2</sub> O <sub>3</sub>		(MnO <sub>2</sub> ), MnO <sub>2</sub> , Mn <sub>2</sub> O <sub>7</sub>
B.			{ Cl <sub>2</sub> O, ClO <sub>2</sub> *, Cl <sub>2</sub> O <sub>7</sub> , I <sub>2</sub> O <sub>5</sub> , I <sub>2</sub> O <sub>7</sub> }
VIII.	{ FeO, Fe <sub>2</sub> O <sub>3</sub> , CoO, Co <sub>2</sub> O <sub>3</sub> , NiO }		[FeO <sub>3</sub> ], CoO <sub>2</sub> , [NiO <sub>2</sub> ]
	RuO, RhO, PdO	{ RuO <sub>2</sub> , Rh <sub>2</sub> O <sub>3</sub> , RhO <sub>3</sub> , PdO <sub>2</sub> , Os <sub>2</sub> O <sub>3</sub> , OsO <sub>3</sub> , Ir <sub>2</sub> O <sub>3</sub> , IrO <sub>2</sub> , PtO <sub>2</sub> }	[RuO <sub>3</sub> ], [Ru <sub>2</sub> O <sub>7</sub> ], (RuO <sub>4</sub> )
	OsO, [IrO], PtO		[OsO <sub>2</sub> ], (OsO <sub>4</sub> )

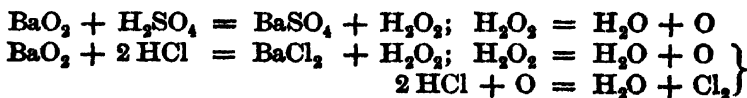
\* Mixed anhydrides.

Oxides in round brackets ( ) belong to more than one type.

or



and with a superoxide



The well-known methods for the preparation of hydrogen peroxide depend, therefore, upon the employment of superoxides, under conditions of temperature and dilution that preclude its decomposition.

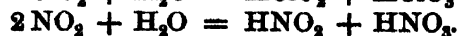
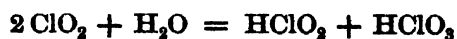
In addition to the above classes of oxides, certain compound oxides are known which are either *mixed anhydrides* or *salts*.

## OF OXIDES

Neutral.	Suboxides.	Saline.	Peroxides.		
			Basic.	Acidic.	Neut.
H <sub>2</sub> O	Cu <sub>2</sub> O, Ag <sub>2</sub> O	Au <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O <sub>2</sub> , K <sub>2</sub> O <sub>4</sub> (AgO) CaO <sub>2</sub> , SrO <sub>2</sub> , BaO <sub>2</sub> CdO <sub>2</sub> , ZnO <sub>2</sub> ν { TiO <sub>2</sub> , ZrO <sub>2</sub> , CeO <sub>2</sub> , Th <sub>2</sub> O <sub>7</sub>		H <sub>2</sub> O <sub>2</sub>
(CO)	Pb <sub>2</sub> O	Pb <sub>2</sub> O <sub>3</sub> , Pb <sub>2</sub> O <sub>4</sub>		[SnO <sub>2</sub> ]	
{ V <sub>2</sub> O <sub>5</sub> , Nb <sub>2</sub> O <sub>5</sub> , Nb <sub>2</sub> O <sub>4</sub> , Ta <sub>2</sub> O <sub>5</sub>					
(N <sub>2</sub> O), NO		Sb <sub>2</sub> O <sub>4</sub> , Bi <sub>2</sub> O <sub>4</sub>	(Bi <sub>2</sub> O <sub>4</sub> )		
(WO <sub>3</sub> )		{ CrO <sub>3</sub> , Mo <sub>3</sub> O <sub>8</sub> , W <sub>3</sub> O <sub>8</sub> , U <sub>3</sub> O <sub>8</sub>	}	CrO <sub>4</sub> , UO <sub>4</sub>	
TeO		Mn <sub>3</sub> O <sub>4</sub> (MnO <sub>2</sub> )	(MnO <sub>2</sub> )	S <sub>2</sub> O <sub>7</sub>	
		Fe <sub>2</sub> O <sub>4</sub> , Co <sub>3</sub> O <sub>4</sub>	Ni <sub>2</sub> O <sub>3</sub>		
(RuO <sub>4</sub> )	Pd <sub>2</sub> O				
(OsO <sub>4</sub> )					

Oxides in square brackets [ ] do not exist, but their derivatives are known.

Mixed anhydrides are acidic oxides which give rise to two acids when they react with water. Such oxides are ClO<sub>2</sub> and NO<sub>2</sub>, which produce chlorous and chloric, nitrous and nitric acids, respectively. Thus:—

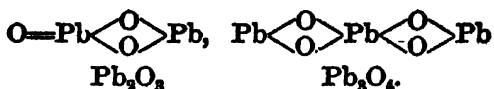


Thus 4 NO<sub>2</sub> is equivalent to N<sub>2</sub>O<sub>3</sub> + N<sub>2</sub>O<sub>5</sub>.

P<sub>2</sub>O<sub>4</sub> is also a mixed anhydride, producing with water, phosphorous and phosphoric acids.

Oxides which are salts are compounds of basic and acidic oxides of the same metal.

Pb<sub>2</sub>O<sub>3</sub> and Pb<sub>2</sub>O<sub>4</sub> are respectively PbO.PbO<sub>2</sub> and 2PbO.PbO<sub>2</sub>, or lead meta- and lead ortho-plumbate;

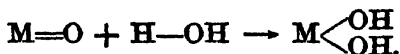


Other examples of this kind are known. They all illustrate the superior acidity of the higher over the lower oxides of a metal, which results in combination between relatively basic and acidic oxides with formation of a salt.

The facts discussed in the above paragraphs are set forth in the scheme of classification of oxides on pp. 60, 61.

### HYDROXIDES

Hydroxides are compounds of oxides with water, formed by the appropriation of the elements of water in the following manner:—



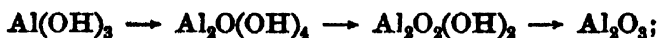
The reaction may be reversible with rise of temperature, the degree of reversibility determining the stability and definiteness of the hydroxide.

Definite hydroxides are to be found amongst the elements of the extreme groups, which possess marked basigenic or oxygenic character. It is these hydroxides which are capable of isolation in the free state, and which display the greatest stability when heated. The oxides of the alkali metals, for instance, readily combine with, and powerfully retain water, with which they form hydroxides freely soluble in water. The oxides of the alkaline earth metals form hydroxides which are less stable than those of the alkali metals, and which retain their water less tenaciously. Magnesium hydroxide is not formed from the oxide by obvious slaking; it is slightly soluble in water, giving an alkaline reaction. The hydroxides of such metals as iron and zinc are not formed directly from the oxides, which are practically insoluble in water and give no alkaline reaction. These hydroxides may, however, be obtained by precipitation, and the basic properties both of the oxides and hydroxides are shown by their power of dissolving in and neutralizing acids,

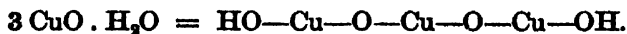
On passing to the non-metallic elements, chemical activity of the oxides and stability of the hydroxides are again met with. Oxides of these elements slake with or are soluble in water, forming hydroxides whose solutions are acid.

Thus the hydroxides of Groups I A and II A are alkalis, that is, they are strong bases, soluble in water; whilst the hydroxides of Groups VII B, VI B, and V B are the strong oxyacids.

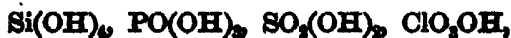
The hydroxide corresponding to an oxide  $\text{MO}_n$  is theoretically  $\text{M}(\text{OH})_{2n}$ , each doubly linked oxygen atom being represented by two OH groups. With basic oxides this maximum hydroxylation is usually realized; thus the oxides  $\text{Li}_2\text{O}$ ,  $\text{BaO}$ ,  $\text{Al}_2\text{O}_3$  correspond to the hydroxides  $\text{LiOH}$ ,  $\text{Ba}(\text{OH})_2$ ,  $\text{Al}(\text{OH})_3$ . Hydroxides of the central members of series of the periodic classification are unstable, especially those of the heavy metals of the eighth group and of silver, gold, and mercury. In some cases intermediate stages of hydroxylation are known. Aluminium hydroxide, for instance, easily loses water in the following stages:—



and cupric hydroxide,  $\text{Cu}(\text{OH})_2$ , passes readily on warming in water into



Hydroxylation of an acidic oxide is seldom complete. The theoretically possible basicity of the acid corresponding to the oxide  $\text{M}_2\text{O}_3$  is three; to the oxide  $\text{MO}_2$  is four; and so on. But, just as the maximum number of hydrogen atoms which can combine with an element is four, so, with one or two exceptions, the maximum basicity of an acid, as measured by the number of hydroxyl groups combined with a non-metallic element, appears to be four. Tetrabasic silicic acid is known to exist, but it is very unstable, and proceeding in series the following are typical acids:—





which correspond to the hydrides



The single definite exception to this rule is furnished by periodic acid, one form of which is  $\text{IO}(\text{OH})_5$ . That iodine forms such a compound, rather than the other halogens, suggests that power of hydroxylation increases with increase of electro-positiveness in a negative group. Confirmation of this idea is found in the case of carbon and silicon, neither  $\text{C}(\text{OH})_4$  nor any of its inorganic derivatives being known. The non-existence of  $\text{NO}(\text{OH})_3$ , as compared with  $\text{PO}(\text{OH})_3$ , further illustrates this point. It must be observed, however, that the power of hydroxylation of a carbon atom is increased by the proximity of negative groups. For whilst  $\text{H}_2\text{C}(\text{OH})_2$  does not exist,  $\text{OC}(\text{OH})_2$  does, though it is unstable; and whilst  $\text{CH}_3\cdot\text{CH}(\text{OH})_2$  is unknown,  $\text{CCl}_3\cdot\text{CHO}$  combines with water, forming  $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$ . In the case of sulphur the basic salts  $\text{Pb}_2\text{SO}_5 (= \text{PbO}, \text{PbSO}_4)$  and  $\text{Hg}_3\text{SO}_6 (= 2 \text{HgO}, \text{HgSO}_4)$  exist; and they may be supposed to be related to  $\text{SO}(\text{OH})_4$  and  $\text{S}(\text{OH})_6$ ; but, inasmuch as they are not directly produced from sulphuric acid, there is no evidence of the existence of the above forms of the acid, although the hydrates  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$  are known.

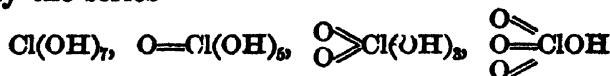
It may be observed that whilst hydroxylation is reduced to its lowest limit in the monobasic oxyacids of the seventh group, in the case of the typical oxides of the eighth group it is non-existent; osmium tetroxide, for example, is incapable of hydroxylation and therefore possesses no acidic properties.

In strict nomenclature the term *ortho*- should be reserved for the fully hydroxylated form of an acid. In practice it has been found convenient to apply it to the most highly hydroxylated salt-forming type. The relationships between the several acids derivable from a single anhydride are best developed by tracing their formation from the hypothetical fully-hydroxylated type by loss of water. Phosphoric anhydride should theoretically give  $\text{P}(\text{OH})_5$  as the true *ortho*-acid; the highest

known acid is  $\text{PO}(\text{OH})_3$ , and this is consequently known as orthophosphoric acid; it is intermediate between the true ortho-acid and metaphosphoric acid; thus:—

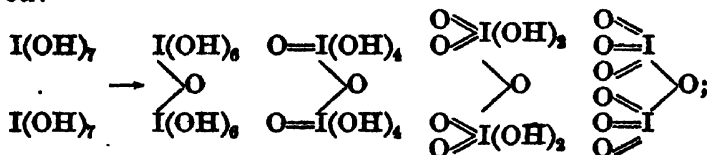


Similarly the series



shows perchloric acid to be in reality the third meta-acid, derived from hypothetical  $\text{Cl}(\text{OH})_7$ . As seen above, the compound  $\text{O}=\text{I}(\text{OH})_6$  exists.

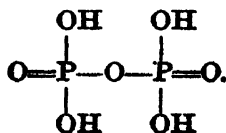
The term *pyro-* or *anhydro-* usually refers to the type of acid which results from dehydration of two or more molecules of the true ortho- or any intermediate form down to the meta-acid. Thus from  $\text{I}(\text{OH})_7$  the following series of acids may be derived:—



the anhydride at last resulting.

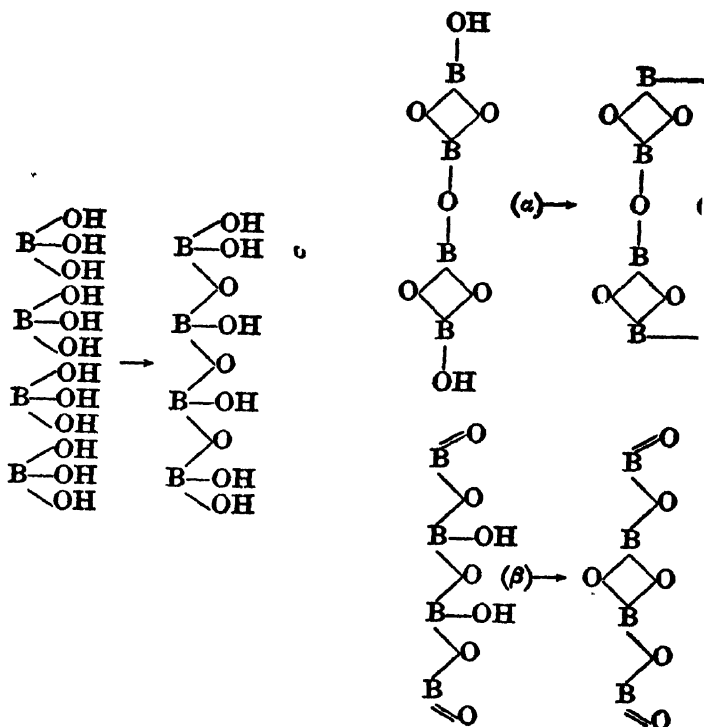
Derivatives of numerous types of periodic acid are known; their ultimate constitution, however, remains undecided.

Pyrophosphoric acid  $\text{H}_4\text{P}_2\text{O}_7$  is the best known acid of this class, its constitution probably being:—



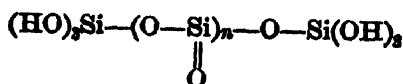
It is possible for more than two molecules of the ortho-acid to participate in this process of dehydration; polymeric metaphosphoric acids thus result (*q.v.*). From four molecules of orthoboric acid the following dehydration products are derivable:—

# INORGANIC CHEMISTRY

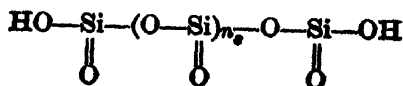


Ordinary borax,  $\text{Na}_2\text{B}_4\text{O}_7$ , is the salt either of  $\alpha$  or  $\beta$  tetraboric acid. The existence of these two formulæ suggests isomerism in the acid and its anhydride; this, however, is unknown, and either pair of formulæ may be taken to represent the constitution of these compounds, so far as present knowledge goes.

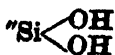
Natural, hydrated silica may similarly be a weak acid of the type



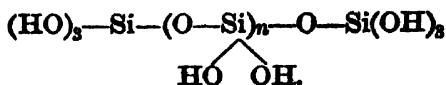
or



Hydration of the "Si=O group to



also renders conceivable the existence of such complex silicic acids as



### SULPHIDES

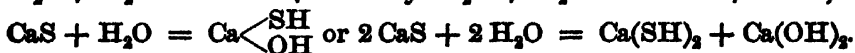
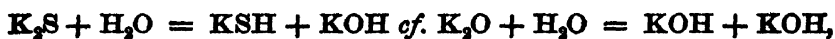
Sulphides possess the same general structure as oxides, and may be classified like them into basic, acidic, neutral, and per-sulphides, representatives of each class occupying corresponding positions in the periodic classification. A sulphide is a binary compound of sulphur with a less electro-negative element; hence the compounds of sulphur with the more electro-negative elements oxygen and chlorine are not sulphides of oxygen and chlorine respectively, but oxides and chlorides of sulphur. The less powerful electro-negative character of sulphur as compared with oxygen serves to account for the difference in properties between oxides and sulphides.

The affinity of a less electro-negative element for oxygen will naturally be superior to its affinity for sulphur, whence follows the very general reaction for the conversion of a sulphide into an oxide by heating or exposure to air, as illustrated in the mode of extracting many metals from their native sulphides. The reaction is determined by the affinity both of the metal and of sulphur for oxygen, as well as by the volatility of sulphur dioxide; it may result in oxidation to sulphate, as in the roasting of lead sulphide, and in the conversion of precipitated copper sulphide into sulphate by exposure in the moist condition to air.

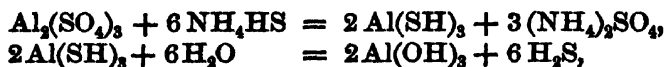
The character of a sulphide may be predicted from that of the corresponding oxide. A metallic sulphide, for instance, will yield salts and sulphuretted hydrogen by the action of acids, thus:—



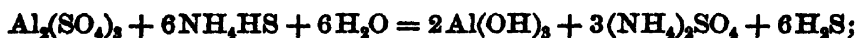
If the oxide is alkaline the sulphide will dissolve in water, forming a mixture of hydrosulphide and hydroxide.



If the oxide is feebly basic the sulphide will be decomposed by water, forming the hydroxide, with evolution of hydrogen sulphide. This is the case with aluminium and chromic sulphides of the type  $M_2S_3$ , which can neither be prepared nor exist in presence of water. Hence ammonium sulphide precipitates hydroxides from solutions of aluminium and chromic salts; thus:—



or



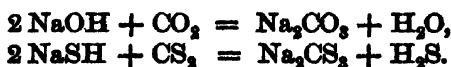
and similarly with chromium.

In the case of ferric salts, ferrous sulphide and sulphur are produced; thus:—



Many acidic oxides have, corresponding to them, sulphides less powerfully acidic than themselves. Thus  $CS_2$  is the thio-anhydride of thio-carbonic acid  $H_2CS_3$ , and dissolves in sodium sulphide solution, forming sodium thio-carbonate.

The following reactions are therefore analogous:—



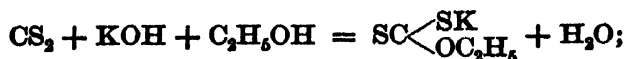
Arsenious sulphide is likewise a thio-anhydride, and dissolves in ammonium sulphide, forming ammonium meta-thioarsenite:



If yellow ammonium polysulphide is used, a meta-thioarsenate is formed:—



When a hydroxide is employed to dissolve a sulphide an oxythiosalt results; thus with potassium hydroxide and alcohol, carbon disulphide gives potassium xanthate,

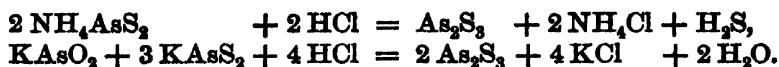


and when arsenious sulphide dissolves in potash, a mixture of arsenite and thio-arsenite is produced; thus:—



Sulphides of antimony and tin behave similarly with alkalis.

By the addition of hydrochloric acid to solutions of these thio- or mixed thio- and oxy-salts, the reaction is reversed and the sulphide is reprecipitated; thus:—



The less powerfully acidic properties of sulphides as compared with oxides are further shown by the easy decomposition of these thio-salts by acids. Few thio-acids indeed are known in the free state.

The formation of superoxides by linkage of oxygen atoms is paralleled among the sulphides by an analogous power of linkage of sulphur atoms. The chain-forming ability of sulphur is, however, superior to that of oxygen; persulphides of the type  $\text{M}_2\text{S}_n$  or  $\text{MS}_n$ , for instance, of the alkali and alkaline earth metals, are easily formed from the simple sulphides by direct combination with sulphur, and these so-called polysulphides—in reality supersulphides—often contain a larger proportion of sulphur than corresponds to oxygen in the superoxide.

When sulphur is boiled with a solution of sodium sulphide the compounds  $\text{Na}_2\text{S}_2$  and  $\text{Na}_2\text{S}_5$  are formed; similarly milk of lime takes up sulphur, forming  $\text{CaS}_2$  and  $\text{CaS}_5$ , and from solutions of these substances  $\text{H}_2\text{S}_2$  and  $\text{H}_2\text{S}_5$  are produced by the action of acids.

There are no oxygen analogues of  $\text{Na}_2\text{S}_5$ ,  $\text{CaS}_5$ , and  $\text{H}_2\text{S}_5$ . At the same time it may be mentioned that there is no oxygen

analogue of the molecule of  $S_8$ , of which these pentasulphides may perhaps be derivatives.

The series of thionic acids, formulated on the general type  $S_x(SO_2.OH)_2$  where  $x=1$  to 3, further illustrates the same tendency to form chains, exhibited by sulphur atoms. Similar oxygen acids,  $O_x(SO_2.OH)_2$ , where  $x=1$  or 2, are known. They are pyro- and persulphuric acid respectively.

## HALIDES

Halides, or binary compounds of the elements fluorine, chlorine, bromine, and iodine with the other elements, are formed by nearly every element, and are, therefore, like oxides, excellently adapted to serve as a basis for comparison of chemical properties.

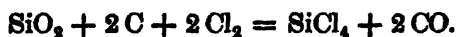
Direct union constitutes a general method of formation of halides. Fluorine combines with every metal and most non-metals, at the ordinary temperature, and the readiness with which combination occurs between a halogen and another element decreases in passing from fluorine to iodine.

The halides of elements giving exclusively basic oxides, that is, halides corresponding to basic oxides, are salts, and are distinguished clearly from halides of electro-negative elements, that is, halides corresponding to acidic oxides. They are produced by the general methods for the preparation of metallic salts; that is, by the action of a metal, oxide or hydroxide, on a halogen acid, or by double decomposition. They are usually non-volatile solids, which are stable on heating but are decomposed by strong sulphuric acid, with liberation of the volatile halogen acid. They are generally soluble in water, though insoluble in non-hydroxylic solvents such as ether, benzene, and chloroform. They undergo electrolytic dissociation in aqueous solution into ions of metal and halogen, and are recoverable unchanged from such solution on evaporation.

These rigorous criteria are true in the fullest sense for the halides of the alkali metals,  $MX$ , alone; but they also apply

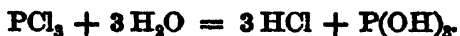
with limitations to the metallic halides,  $MX_2$ , especially to  $BaX_2$ .

The properties of a halide of a typically non-metallic or electro-negative element are essentially different from the above. Halides of this class are usually obtained by direct union of the elements, or, in the case of chlorides, by passing chlorine over a heated mixture of an oxide of the element and carbon. This is a method particularly useful for obtaining chlorides of the less electro-negative of the non-metals, as, for example, silicon.



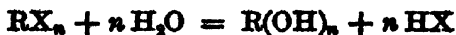
Typical non-metallic halides are stable when heated, but are easily volatile, often being liquids or solids of low melting-point. They are soluble in non-hydroxylic solvents, and are unaffected by strong sulphuric acid; they have a pungent odour, and are decomposed by water, giving mixtures in solution of halogen acid and oxyacid corresponding to the oxide analogous to the halide.

These properties are well illustrated by the chlorides of phosphorus, which are readily acted on by water, heat being generated, and a solution of halogen acid and a corresponding acid of phosphorus being formed. Thus:—



Mendeléeff uses the term *chloranhydrides* for such chlorides as yield oxyacids on complete decomposition by water; a convenient general term inclusive of all such analogous halides would be *halanhydrides*. Thus  $PCl_3$ ,  $SiCl_4$ ,  $PBr_3$ ,  $SF_6$  are halanhydrides; and the oxyacids formed by their decomposition by water are phosphorous, silicic, phosphoric, and sulphuric acids, halogen hydracid being produced at the same time.

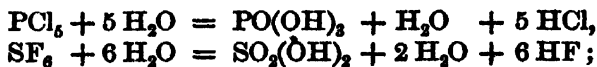
Since the general reaction



is here involved, the oxyacid formed might be expected to contain as many hydroxyl groups as the halanhydride con-



tained halogen atoms, the latter being the ortho-halide of the acid. With the highest halides of phosphorus and sulphur, as well as in other cases, this is not so, the true ortho-acids,  $P(OH)_5$  and  $S(OH)_6$ , being unknown. Consequently, when these halides react with water the following changes take place:—

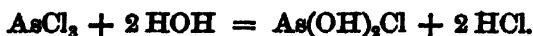


$POCl_3$ , and probably oxyhalides of sulphur, being formed as intermediate products in the reaction.

The halides of phosphoric and sulphuric acids respectively are  $POX_3$  and  $SO_2X_2$ ; but these compounds are oxyhalides of the elements, and are better not described as halanhydrides, this term being reserved for the halides of true ortho-acids, which at the same time are halides of non-metallic elements.

It appears from the consideration of  $PCl_5$  and other non-metallic chlorides that full chlorination is more easily realizable than full hydroxylation. As before observed, inability to retain in stable union the maximum possible number of hydroxyl groups is a general characteristic of a non-metallic atom.

The halides of metals whose hydroxides are feeble bases—in some instances behaving as acids in relation to strong alkalis—are of an intermediate character, falling between the true metallic salt and the true halanhydride. They are distinguished often by being more volatile than the true metallic halides, but particularly by their ready decomposition by water, with production of oxy- or basic halides. Aluminium chloride is a good example of such a halide. It is an easily volatile solid which dissolves in water with evolution of heat and partial hydrolysis; on evaporation of the solution the oxide remains. Arsenious chloride is likewise an interesting example. It is a liquid, the first action of cold water upon which is as follows:—



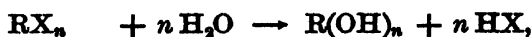
On warming with water the hydrolysis is completed,  $As(OH)_3$  being formed. The compound  $As(OH)_2Cl$  may be regarded

either as a basic salt or a chloro-acid, from one or other point of view.

Not only are aluminium, arsenious, and similar halides decomposed by water, but they are generated from the hydroxides by excess of halogen acid; these two changes being represented by the reversible reaction,



This reversibility is on account of the intermediate character of such halides between halanhydrides and salts; the non-reversible reaction,

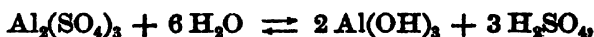


being characteristic of halanhydride decomposition, and the non-reversible reaction,



of salt-formation.

Comparable with the halides are the oxysalts. For instance, aluminium sulphate undergoes hydrolytic dissociation according to the following reaction:—



a basic salt being in fact produced; but potassium sulphate, a true salt, is not hydrolysed by water.

Many halides, in particular fluorides and chlorides of non-metals and weak metals, display the property of readily yielding double or complex salts with metallic halides, and more or less stable acids by union with halogen acids in solution. Such are  $PtCl_2$  giving  $K_2PtCl_4$ ,  $PtCl_4$  giving  $K_2PtCl_6$ , and  $H_2PtCl_6 \cdot 6 H_2O$ ,  $AuCl_3$  giving  $KAuCl_4$ ,  $AuBr_3$  giving  $KAuBr_4$ , the fluorides of silicon, germanium, and tin giving  $K_2XF_6$ , and  $BF_3$  giving  $KBF_4$ . This property is comparable with that of the formation of double or complex cyanides by many metallic cyanides; especially those of the eighth group (*q.v.*).

It may be suggested that the union of basic and acidic

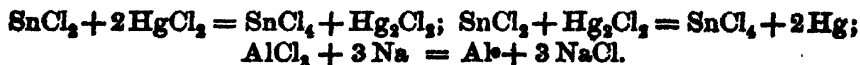
halides to form complex salts is analogous on the one hand to combination between basic and acidic oxides to form simple salts, and on the other hand to union between sulphates such as those of potassium and aluminium with the formation of alums and other double salts.

## CHAPTER IV

### OXIDATION AND REDUCTION

The processes of oxidation and reduction are amongst the most widely occurring general reactions of chemistry. Their consequent value for comparative purposes, and the light which they throw upon the mechanism of many reactions, obscure from other stand-points, render it desirable to consider the mechanism and more general reactions of these processes.

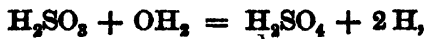
As a first approximation the following definitions may be given:—Oxidation consists in the combination of oxygen with an elementary or compound substance. Reduction is the converse process, or the withdrawal of oxygen from a substance containing it. Necessary limitations and extensions at once suggest themselves. Loss of oxygen by the application of heat, and decomposition by the agency of the electric current, although of the nature of reduction, are scarcely to be classed as examples of this process. Further, the addition or abstraction of oxygen is not the sole characteristic of these reactions. Some other element, notably chlorine, or a complex acidic radicle, may be the component added or withdrawn, as in cases of reduction of metallic chlorides either to lower chlorides or to metals, for example, in the reactions:—



The chlorination of a metal or chloride is generally possible by the direct action of chlorine alone, as in the production of  $\text{SnCl}_4$  from  $\text{SnCl}_2$  and  $\text{HgCl}_2$  from  $\text{Hg}_2\text{Cl}_2$ , the element added

itself performing a function analogous to oxidation; just as oxygen may oxidize a metal to an oxide, or a lower to a higher oxide.

In some cases, abstraction or addition of hydrogen may constitute oxidation or reduction respectively. Reduction of an organic dye substance by sulphurous acid is due to this cause, as is shown by the following reaction:—



hydrogen being added on to the colouring matter with production of a leuco-compound.

A well-known instance of this mode of action with organic compounds is furnished by the interconversion of ketones and secondary alcohols.<sup>1</sup>



In the case of the complex cyanides, for instance potassium ferro- and ferricyanide, the electro-negative radicle '(CN) may behave similarly to Cl in respect to oxidation and reduction processes. Passage from ferrocyanide,  $\text{K}_4\text{Fe}(\text{CN})_6$ , to ferricyanide,  $\text{K}_3\text{Fe}(\text{CN})_6$ , involves essentially a change from  $\text{Fe}(\text{CN})_2$  to  $\text{Fe}(\text{CN})_3$ , parallel to the conversion of  $\text{FeCl}_2$  into  $\text{FeCl}_3$ , or  $\text{FeO}$  into  $\text{Fe}_2\text{O}_3$ , and is therefore to be classed as an oxidation process.

*Oxidation* may therefore be described as the conversion of a compound representing a lower into one representing a higher stage of combination with oxygen, by the addition either of oxygen, or an equivalent electro-negative atom or radicle, or by the removal of hydrogen or an electro-positive atom or radicle.

*Reduction* may be defined as the result of the converse operations.

Among inorganic compounds, oxidation usually denotes an increase in the active valency of the central atom, as in

<sup>1</sup> Organic oxidation processes, resulting in the abstraction of hydrogen, are, however, best considered as proceeding through the intermediate addition of oxygen. This is the case in the oxidation of secondary alcohols, as is shown by the scheme



examples already given. Increase of valency is not, however, a necessary concomitant of oxidation; for no such increase takes place in the conversion of an oxide into a superoxide, for instance,  $\text{BaO}$  into  $\text{BaO}_2$ , or  $\text{H}_2\text{O}$  into  $\text{H}_2\text{O}_2$ .

*Oxidizing and Reducing Agents.*—To effect the changes discussed above, certain chemical substances are employed as oxidizing or reducing agents. An *oxidizing agent* may be defined, in most general terms, as a substance, elementary or compound, capable of increasing the proportional content in electro-negative atoms or groups of the molecule of a given substance, either by actual increase in the number of such atoms or groups within the molecule, or by the removal of a more electro-positive component.

The converse proposition defines a *reducing agent* as a substance capable of decreasing the proportion of electro-negative atoms or groups within the molecule of an element or compound.

An oxidizing agent is therefore an element or compound possessing affinity for, and easily combining with, an electro-positive element or group.

A reducing agent is similarly a substance possessing affinity for an electro-negative atom or group.

In the operation of a reagent of either kind, reduction is suffered by the oxidizing agent, and oxidation by the reducing agent. The most powerful oxidizers are therefore characterized by ready reducibility, and the most powerful reducers by ready oxidizability.

Among the *common oxidizing agents* may be enumerated oxygen, ozone, peroxides, oxyacids such as nitric acid, the halogens with their oxyacids and their salts, and acids corresponding to higher metallic oxides, such as chromic and permanganic acids and their salts; also certain unstable basic oxides, such as those of silver and gold. All these substances operate by the direct addition of oxygen. Chlorine operates either by the liberation of oxygen ( $2\text{Cl} + \text{H}_2\text{O} = 2\text{HCl} + \text{O}$ ), by direct chlorination, or by the abstraction of hydrogen or a metal.

Common reducing agents are:—hydrogen, gaseous and so-called nascent, unstable hydrides, such as hydriodic acid and the hydrides of sulphur, selenium, tellurium, phosphorus, arsenic, antimony, and

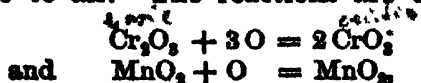
*silicon*; *carbon*; many metals, such as *sodium*, *potassium*, *magnesium*, which act by virtue of their affinity for oxygen or other electro-negative elements; lower oxides, such as *carbon monoxide*, and lower oxyacids and salts, such as *hypophosphites*, *phosphites*, and *sulphites*; salts, such as *potassium cyanide* and *formate*, which combine directly with oxygen under certain circumstances; and lower salts, such as *ferrous*, *chromous*, and *stannous salts*.

## MODES OF APPLICATION AND MECHANISM

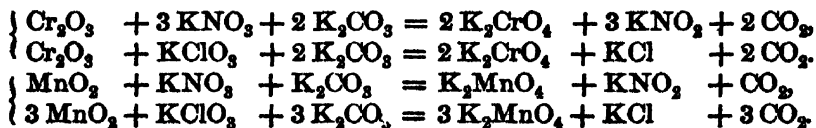
### *Oxidation in the Dry Way*

Oxidation may be effected in the dry way with the aid of heat. The production of oxides, and of some higher oxides from lower oxides, by direct union, illustrates this method. Examples are the production of an oxide by heating an element such as sulphur, phosphorus, sodium, magnesium, zinc, mercury, lead, or iron in air or oxygen, and the formation of certain higher oxides, such as red-lead,  $\text{Pb}_3\text{O}_4$ , and barium peroxide,  $\text{BaO}_2$ , by heating the lower oxides,  $\text{PbO}$  and  $\text{BaO}$ , in air.

Oxidation by fusion, or powerful heating with highly oxygenated salts, belongs to the same category; for instance, the action of potassium chlorate or nitrate on sulphur, sulphides, and carbon. The production of acidic from basic oxides by this process is of importance analytically and technically. Such acidic oxides are often unstable when heated in the free state, and therefore are not formed by the direct union of basic oxides with oxygen. The presence of caustic alkali or carbonate renders the oxidation by chlorate, nitrate, or atmospheric air at high temperature permanent by the formation of a stable salt of the higher oxide. This process is best illustrated by the oxidation of chromic oxide and manganese dioxide by fusion with alkali, together with an oxidizing agent, or with free exposure to air. The reactions are essentially



chromate and manganate, *e.g.*  $\text{K}_2\text{CrO}_4$  and  $\text{K}_2\text{MnO}_4$ , being produced in the actual operation. The nitrate or chlorate employed itself undergoes reduction to nitrite or chloride, so that the following equations represent the complete reactions:—



Certain peroxides, such as those of lead and sodium, are useful as oxidizing agents in the dry way. Organic substances containing sulphur and phosphorus are oxidized when heated with excess of sodium peroxide, with formation of sodium sulphate, and phosphate.

Dry ozone oxidizes mercury and silver superficially at atmospheric temperature.

#### *Oxidation in the Wet Way*

Some substances are oxidized by atmospheric oxygen at ordinary temperature in presence of moisture. When phosphorus or iron borings are placed in contact with air and water in an enclosed space they gradually absorb the oxygen. The rusting of iron appears to be accelerated by the presence of carbon dioxide, and the corroding of lead consists in the formation of hydroxide in solution; thus,  $2\text{Pb} + 2\text{H}_2\text{O} + \text{O}_2 = 2\text{Pb}(\text{OH})_2$  and its precipitation as basic carbonate by the carbon dioxide present.

Ozone oxidizes certain substances in solution; for instance, it liberates iodine from potassium iodide,



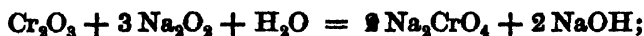
it also bleaches various colouring matters by oxidation, but reduces hydrogen peroxide thus:—



Hydrogen peroxide likewise behaves both as an oxidizing and as a reducing agent; its oxidizing action is generally

manifested in neutral or alkaline solution; for instance, lead sulphide suspended in water is oxidized to sulphate,  $\text{PbS} + 4 \text{H}_2\text{O}_2 = \text{PbSO}_4 + 4 \text{H}_2\text{O}$ , and iodine is liberated from potassium iodide; as with ozone, various basic oxides are changed to peroxides.

Sodium peroxide oxidizes chromic oxide in presence of water, producing chromate,



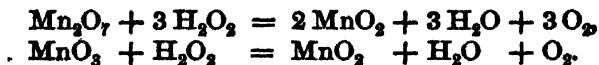
lead peroxide behaves in a similar way in presence of alkali,



Sodium peroxide also oxidizes alkali sulphides to sulphates in solution,

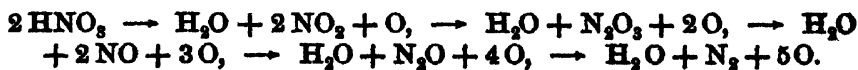


and manganous compounds to hydrated manganese dioxide. Manganese compounds are not raised to a higher stage of oxidation than this by sodium peroxide in solution, since hydrogen peroxide is generated, which, under these circumstances, would reduce permanganates and manganates to manganese dioxide; thus:—



Oxyacids owe their oxidizing powers to the ease with which they part with oxygen.

Nitric acid suffers reduction in the following stages:—



Hydroxylamine and ammonia may likewise be produced; thus:—

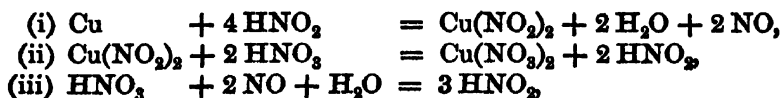


This acid may be used in a diluted or concentrated condition to oxidize metals or non-metals, oxides, sulphides, salts, and organic matter.



The nature of the reduction product depends upon the relative concentrations of acid and reducing agent, as well as upon the nature of the latter.

The mechanism of reduction of nitric acid by metals may here be discussed. Two views at first sight appear possible: either that nascent hydrogen is liberated from the acid by the metal, which in turn reduces more of the acid, or that the metal itself reduces the acid directly. Now the metals silver, mercury, copper, and bismuth have no perceptible action on cold, dilute sulphuric or hydrochloric acids; it is therefore unlikely that they will reduce nitric acid by the generation and agency of nascent hydrogen. As a matter of fact they have no action on cold, dilute nitric acid. If, however, the acid contains a trace of nitrous acid, or a lower oxide of nitrogen, or is warmed so as to induce incipient decomposition, action at once commences with evolution of nitric oxide and formation of metallic nitrate. The following reactions probably take place with copper, and similarly with the rest of these metals:<sup>1</sup>—



or adding



So, by the catalytic action of a small amount of nitrous acid, this acid is being continuously produced; it is not, however, stable, but decomposes at once thus:—



so that nitric oxide is evolved, and a nitrate of the metal appears in solution.

Those more electro-positive metals, which displace hydrogen perceptibly from dilute sulphuric acid and concentrated or dilute hydrochloric acids, may be supposed capable of reducing nitric acid through the agency of nascent hydrogen. They

<sup>1</sup> Voley, *Roy. Soc. Trans.* (1891), 182, A. 279-317.

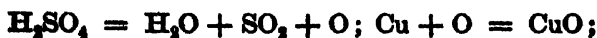
are magnesium, zinc, cadmium, iron, aluminium, tin, and lead. Whilst the former metals, silver, mercury, copper, and bismuth never reduce nitric acid to hydroxylamine or ammonia, those latter may produce these substances besides nitrous oxide and nitrogen (probably resulting from the interaction of nitrous acid and ammonia). Hydrogen itself, indeed, is among the gases evolved from dilute nitric acid by magnesium. It would be difficult to say how far nascent hydrogen and how far the metal itself is responsible for the reduction to nitrous acid and lower compounds; in the formation of ammonia nascent hydrogen must, however, play a part. Dilute nitric acid is reduced to ammonia by the zinc-copper couple, and also by iron filings in the presence of a little sulphuric acid.

Nitrogen peroxide appears as a reduction product of nitric acid in certain cases, notably in the oxidation of red phosphorus, arsenious oxide, and organic compounds. It is also produced when moderately strong nitric acid reacts with metallic tin. In this case, however, it is not entirely a reduction product of nitric acid, for the stannic nitrate first produced is unstable, and breaks up thus:—



Thus when the metal has feebly electro-positive properties its most stable oxide is produced instead of the nitrate. Similarly antimony is oxidized to  $\text{Sb}_2\text{O}_4$ , and, passing to non-metals, phosphoric acid corresponding to  $\text{P}_2\text{O}_5$ , arsenic acid corresponding to  $\text{As}_2\text{O}_5$ , and iodic acid corresponding to  $\text{I}_2\text{O}_5$  are produced. Sulphur is converted into sulphuric acid, but bromine and chlorine are not acted on by nitric acid.

Sulphuric acid also may act as an oxidizing agent. Metals which do not decompose steam on moderate heating, nor give hydrogen with dilute acids, as well as many that do both, are oxidized by hot strong sulphuric acid. Thus with copper:—



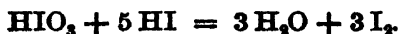
or



Some of the copper sulphate formed is generally reduced to sulphide by the excess of metallic copper. With carbon, sulphur dioxide and carbon dioxide are produced thus:—

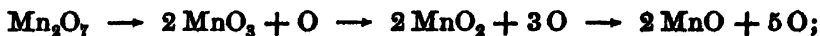


Chloric, bromic, and iodic, as well as perchloric and periodic acids, and the oxides of chlorine and iodine, are oxidizing agents, the available oxygen being represented by the state of oxidation in which the halogen exists in these compounds above the condition of halide. Thus, for instance, iodic and hydriodic acids react upon one another as follows:—



Oxidation by aqueous solutions of hypochlorites, hypobromites, and hypiodites results from the ready decomposition of these salts,  $\text{NaXO} = \text{NaX} + \text{O}$ ; a very good example being the oxidation of ammonia and amides such as urea to nitrogen; thus these compounds constitute a source of available oxygen, which may be obtained in the free state by the catalytic action of cobaltous oxide on bleaching-powder solution.

Oxidation by means of chromates or dichromates and permanganates is due to the difference in oxygen content between the acidic and basic oxides  $\text{CrO}_3$  and  $\text{Cr}_2\text{O}_3$ , and  $\text{Mn}_2\text{O}_7$  and  $2 \text{MnO}$ , respectively. In the case of permanganates, however, there are several stages of reduction, thus:—

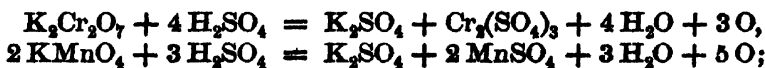


which become apparent more especially when the reaction takes place in alkaline solution. Thus green alkali manganate, such as  $\text{Na}_2\text{MnO}_4$ , is produced by the action of mild reducing agents in cold alkaline solution; in neutral solution, or by more vigorous reduction promoted by heating, hydrated manganese dioxide is precipitated. This substance may be further reduced if a more stable product thus results; for instance, when dilute potassium permanganate solution is added to excess of solution of alkali sulphide and free alkali, the hydrated manganese dioxide first precipitated is converted into more stable manganous sulphide, the alkali sulphide being simultaneously

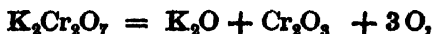
oxidized to sulphate. In acid solution these successive stages of reduction are not so well marked, since the stable condition of soluble manganous salt is more easily reached. In some cases, however, the momentary formation of hydrated manganese dioxide can be observed; also the manganous salt formed in the reaction sometimes assists oxidation by itself becoming alternately oxidized to the dioxide and again reduced. This is the case in the oxidation of warm acidified oxalate solutions by permanganate.

Chromates and dichromates show no such intermediate stages in reduction; in acid solution chromic salts result, in neutral or alkaline solution basic chromic salts or hydrated chromic oxide itself. Owing to their great instability, chromous salts are only produced by powerful reduction in absence of air.

Considering the oxidizing action of potassium dichromate and potassium permanganate in dilute sulphuric-acid solution, the reactions may thus be represented:—



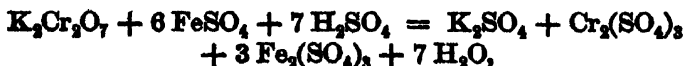
these equations being derived from the more simple expressions



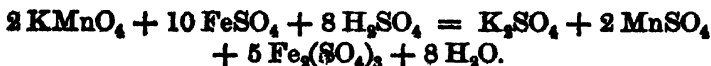
and



The oxidation of ferrous sulphate,  $\text{FeSO}_4$ , to  $\text{Fe}_2(\text{SO}_4)_3$  may serve as an example. Since  $2\text{FeO} + \text{O} = \text{Fe}_2\text{O}_3$ , the complete equations become:—



and



Both of these reagents liberate iodine from potassium iodide, oxidize sulphurous to sulphuric acid, together with some dithionio acid,  $\text{H}_2\text{S}_2\text{O}_6$ , in the case of permanganate, and hydrogen sulphide to water and sulphur, together with some

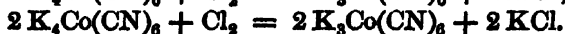
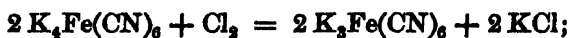
sulphuric acid. Acidified permanganate solution likewise reacts with hydrogen peroxide thus:— $\text{H}_2\text{O}_2 + \text{O} = \text{H}_2\text{O} + \text{O}_2$ , and oxidizes oxalic acid thus:— $\text{H}_2\text{C}_2\text{O}_4 + \text{O} = \text{H}_2\text{O} + 2\text{CO}_2$ . The complete equations for these reactions, when occurring singly, may be constructed according to the principle illustrated above.

Permanganic acid is less stable, and therefore more likely to bring about oxidation than chromic acid. This distinction is seen in the different rates with which the two substances oxidize hydrogen sulphide, and in their different behaviour towards hydrochloric acid. Both can oxidize this substance, causing chlorine to be evolved, but whilst considerable concentration and heat are necessary in the case of chromic acid, permanganic acid slowly oxidizes cold dilute hydrochloric-acid solution.

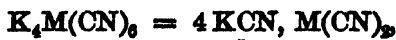
Chlorine may oxidize, either by direct union, as in the conversion of ferrous into ferric chloride,  $2\text{FeCl}_2 + \text{Cl}_2 = 2\text{FeCl}_3$ ; or by causing the addition of oxygen or other electro-negative radicles, as, for instance, in the conversion of nickelous into nickelic hydroxide in presence of alkali,



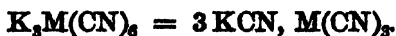
a reaction identical with that effected by hypochlorite. Oxidation may, however, consist in the removal of hydrogen or a metal, as in the conversion of ferro- into ferri- and cobalto- into cobaltic-cyanides:



These reactions, however, really consist in the change of ferrous and cobaltous into ferric and cobaltic compounds, since



and



Silver oxide acts as an oxidizing agent in those cases in which it is reduced to metallic silver. Among the best-known examples are the oxidation of tartrates, formates, and glucose

in solution, with the precipitation of a silver mirror on the sides of the containing vessel.

*Reduction in the Dry Way*

Reduction reactions carried out in the dry way are of great importance in the isolation of free elements, and in particular the metals. Typical cases are indicated by the following equations:—

- (1)  $\text{K}_2\text{CO}_3 + 2\text{C} = 2\text{K} + 3\text{CO}.$
- (2)  $4\text{KOH} + 3\text{Fe} = 4\text{K} + \text{Fe}_3\text{O}_4 + 2\text{H}_2.$
- (3)  $\text{AlCl}_3 + 3\text{Na} = \text{Al} + 3\text{NaCl}.$
- (4)  $\text{Na}_2\text{SiF}_6 + 4\text{Na} = \text{Si} + 6\text{NaF}.$
- (5)  $\text{SnO}_2 + 2\text{C} = \text{Sn} + 2\text{CO}.$
- (6)  $\text{Fe}_3\text{O}_4 + 4\text{C} = 3\text{Fe} + 4\text{CO}.$
- (7)  $\text{CoO} + \text{H}_2 = \text{Co} + \text{H}_2\text{O}.$
- (8)  $2\text{AgCl} + 2\text{Hg} = 2\text{Ag} + \text{Hg}_2\text{Cl}_2.$
- (9)  $\text{Cr}_2\text{O}_3 + 2\text{Al} = 2\text{Cr} + \text{Al}_2\text{O}_3.$
- (10)  $2\text{PbO} + \text{PbS} = 3\text{Pb} + \text{SO}_2 \text{ and } \text{PbSO}_4 + \text{PbS} = 2\text{Pb} + 2\text{SO}_2.$

A large number of well-known metallurgical operations are included in the above reactions. Reaction (9), which is applicable to ferric as well as chromic oxide, is known as Goldschmidt's reaction; it proceeds spontaneously when started by means of a fuse, on account of the large amount of heat developed in the process.

*Reduction in Solution*

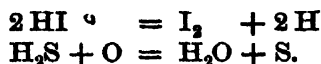
A large number of reductions take place in solution.

The action of nascent hydrogen is illustrated in the reduction of ferric to ferrous salts by the abstraction of 'Cl or "SO<sub>4</sub>; of chlorates and nitrates to chlorides and nitrites or lower compounds, by zinc and dilute acids; and in the reduction of organic compounds by such reagents as zinc dust and water or acid, tin and hydrochloric acid, sodium and aluminium amalgams, and sodium and amyl alcohol.

Reducing salts and analogous compounds operate by virtue of their conversion into a compound of higher electro-negative content; for instance,  $\text{SnCl}_2$  to  $\text{SnCl}_4$  and  $\text{FeCl}_2$  to  $\text{FeCl}_3$ ; or else by their conversion into a more highly oxygenated salt.

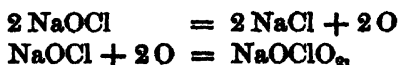
Thus sulphurous acid and sulphites are oxidized to sulphuric acid and sulphates by the reduction of ferric salts, nitric acid, and iodic acid with liberation of iodine.

The hydrides enumerated in the list of reducing agents act in consequence of their instability, or of the superior affinity of their hydrogen for oxygen or chlorine. Hydriodic acid and hydrogen sulphide represent the two classes respectively; thus:—

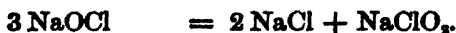


An interesting case of reduction, which has already been mentioned, is that of the mutual decomposition of two oxidizers, the evolution of oxygen resulting. Thus hydrogen dioxide and ozone decompose one another,  $\text{H}_2\text{O}_2 + \text{O}_3 = \text{H}_2\text{O} + 2\text{O}_2$ ; and hydrogen dioxide and acidified permanganate, as before observed.

Simultaneous oxidation and reduction of a single substance is a phenomenon of common occurrence. The oxidation is sometimes effected by the substance itself, and may be termed "self-oxidation". This process is illustrated by the following reactions. When hypochlorites are heated in solution, chlorides and chlorates result, the chlorate being an oxidation product of the hypochlorite, and formed by combination with oxygen derived from another portion of the hypochlorite; thus:—



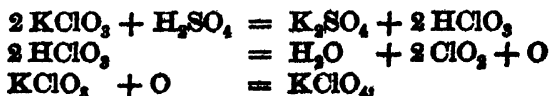
or



The generation of potassium perchlorate from chlorate by the action of heat may be explained by the same principle:—



and also the formation of chlofine peroxide and potassium perchlorate by the action of sulphuric acid:—



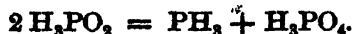
whence



Phosphorous acid when heated gives by self-reduction and oxidation phosphine and phosphoric acid,



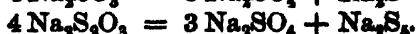
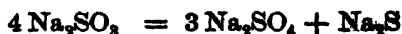
Hypophosphorous acid behaves similarly,



Nitrous acid undergoes spontaneous change in aqueous solution into nitric acid and nitric oxide:—



and alkali sulphite and thio-sulphate pass on ignition in absence of air into sulphate and sulphide and polysulphide respectively:—



## CHAPTER V

### GROUP I

#### SUB-GROUP A

	Li (6·94)
	Na (23·00)
K	(39·10)
Rb	(85·45)
Cs	(132·81)

#### SUB-GROUP B

Cu	(63·57)
Ag	(107·88)
<hr/>	
Au	(197·2).

The typical elements, lithium and sodium, together with the three members of the A sub-group, potassium, rubidium, and caesium, form the natural family of the alkali metals. These elements are closely related to one another, and show a regular gradation both of physical and chemical properties.

The elements of the B sub-group, copper, silver, and gold,



display very little resemblance to the metals of the alkalis, in many respects, indeed, offering a marked contrast to these metals. By the position which they occupy, however, they are seen to be related on the one hand to the metals of the eighth group, nickel, palladium, and platinum, and on the other to zinc, cadmium, and mercury, the members of sub-group II B. The reality of these relationships, as will be seen later, justifies the position of these three elements in sub-group I B. At the same time it may be pointed out that, in accordance with the provisions of the periodic law, the divergence in properties between similarly related elements of A and B sub-groups is greatest in the extreme groups I and VII, being least in Group IV.

### THE ALKALI METALS

The natural modes of occurrence of these metals suggest analogies between them. Thus lithium occurs together with sodium and potassium in certain phosphates and silicates, as well as in mineral waters and in plants; sodium and potassium occur together in feldspar and other silicates, as well as in the Stassfurt deposits in the form of chlorides; rubidium and caesium, likewise, are found in mineral waters at Stassfurt, and in silicates which may also contain lithium, sodium, and potassium. Some specimens of lepidolite, or lithia mica, contain all the alkali metals. Whilst sodium and potassium compounds are abundant, lithium compounds are somewhat, and rubidium and caesium compounds very rare. The metals are obtained by the electrolysis of their chlorides or hydroxides, or, with the exception of lithium, which is only volatile at high temperature, by the reduction of their oxides by heating with carbon, or such metals as iron, aluminium, and magnesium. The following are the chief physical properties of these metals:—

	Li	Na	K	Rb	Cs
Dens. ....	0.534	0.971	0.862	1.532	1.87
At. Vol. ....	13.0	23.7	45.4	55.8	70.1
M.P. ....	186°	98.6°	62.5°	38.5°	28-27°
B.P. ....	Very high	742°	667°	?	270°

The metals and their salts colour the Bunsen flame and give spectra which contain few lines. Since the same spectra are obtained from the metals and their salts, it is concluded that the latter are dissociated in the flame.

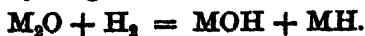
A comparison of these physical properties reveals important gradations from lithium to caesium. These metals are characterized by low density and correspondingly high atomic volume, so that they stand at the apices of the atomic volume curve of Lothar Meyer. Moreover, although the densities increase from lithium to sodium, their ratio of increase is not so great as with the atomic weights, so that a regular and considerable rise in atomic volume occurs throughout the group. The interpretation which must be given to the large atomic volumes of these elements is that the interspaces between the atoms in the solids are large when compared with the size of the atoms themselves. Mendeléeff attributes the chemical activity of the elements to this cause, and this is consistent with the increase in chemical activity with rise in atomic volume from lithium to caesium.

The most striking chemical property of these metals is the affinity which they manifest for oxygen. This is illustrated by the difficulty of reduction of the oxides, but more especially by the fact that the metals tarnish when exposed to air, and decompose water with evolution of hydrogen. Owing to its high melting-point lithium does not fuse under these circumstances; sodium, however, fuses; and potassium, rubidium, and caesium, owing to the superior heat of their reaction with water, cause inflammation of the evolved hydrogen.

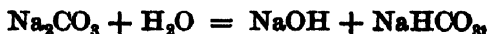
#### OXIDES ( $M_2O$ ) AND HYDROXIDES ( $M'OH$ )

The typical oxides,  $M_2O$ , of the alkali metals are crystalline solids deepening in colour from lithium oxide, which is white, to caesium oxide, which is orange-red. Lithium oxide is obtained by heating the hydroxide in a current of hydrogen; the others by partial oxidation of the metal in pure, dry oxygen, the remaining unchanged metal being distilled off in a vacuum.

They react with water to form the hydroxides, and, excepting lithium, with hydrogen to form hydroxides and hydrides:



The hydroxides are deliquescent, except lithium hydroxide, and form crystalline masses whose aqueous solutions are strongly alkaline, and readily absorb carbon dioxide from the air. These properties are those of typical basic oxides and hydroxides, which show no acidic properties whatever; and associated therewith are certain characteristic properties of salts. Alkali halides and sulphates do not undergo hydrolytic dissociation, so that their aqueous solutions are neutral in reaction.<sup>1</sup> Solutions of such salts as the phosphates, carbonates, and borates, derived from weaker acids, are alkaline in reaction, hydroxyl ions preponderating after hydrolysis on account of the superior electrolytic dissociation of the base over the acid. Even a solution of  $Na_2HPO_4$  is alkaline on this account, and a solution of  $Na_2CO_3$  is hydrolysed thus:—



the NaOH producing a preponderance of hydroxyl ions. It is doubtful, indeed, whether the solution of any normal phosphate, carbonate, or borate possesses a neutral reaction, salts of these acids and less powerful bases being generally insoluble in water.

Another characteristic of the alkali metals depending upon their powerfully basigenic properties is their power of forming stable acid salts, such as  $M'HSO_4$  and  $M'HCO_3$ . The properties of bicarbonates are specially instructive, since those of the alkalis alone exist in the solid state, though the alkaline earth and magnesium bicarbonates are known in solution. Even the alkali bicarbonates are decomposed by boiling water, as also are those of the alkaline earths and magnesium. The power to form bicarbonates is possessed only by the most powerful metals; normal carbonates, indeed, being formed by comparatively few metals, so great is the tendency for carbonic dioxide to be lost and a basic carbonate to be produced. The

<sup>1</sup> Lithium chloride is somewhat hydrolysed by water.

alkali metals do not form basic carbonates or any basic salts, their oxides being sufficiently basic to retain the full complement even of the weakest acid.

#### SUB-OXIDES AND SUB-SALTS

Various sub-oxides, such as  $\text{Na}_4\text{O}$  and  $\text{K}_4\text{O}$ , have been described, but their existence is doubtful. The sub-chlorides  $\text{Na}_2\text{Cl}$  and  $\text{K}_2\text{Cl}$  are said to be grayish-blue in colour; the blue colour of certain naturally occurring specimens of sodium chloride is attributed to the presence of sub-chloride. These compounds are probably formed by heating the metals with the chlorides in a stream of hydrogen, or by the electrolysis of the fused chlorides themselves; and are decomposed by water thus:—



#### PEROXIDES

Of the peroxides, the compounds  $\text{Na}_2\text{O}_2$  and  $\text{K}_2\text{O}_4$  are the best known, though peroxides of the other alkali metals exist.

**Sodium Peroxide**,  $\text{Na}_2\text{O}_2$ , is formed when sodium is ignited in a stream of oxygen. It is a yellowish-white solid which forms with water the crystallo-hydrate  $\text{Na}_2\text{O}_2 \cdot 8 \text{H}_2\text{O}$ . It is a true superoxide, and possesses a constitution analogous to that of hydrogen peroxide, since it yields this substance, together with sodium hydroxide, when dissolved in water.

When sodium peroxide is acted on by a solution of hydrogen chloride in alcohol, or with absolute alcohol at  $0^\circ$ , the following reaction takes place:—

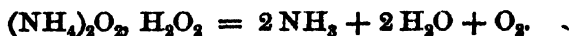


the latter substance remaining as a white powder, known as sodyl hydroxide. Although decomposed by mineral acids, this substance combines with acetic acid to form the sodium salt of peracetic acid,  $\text{NaOOCOCH}_3$ .

Potassium is not known to form a dioxide corresponding to  $\text{Na}_2\text{O}_2$ , but when the metal burns in oxygen the tetroxide

$K_2O_4$  is produced. The existence of such a high oxide is remarkable, and probably unique; this compound is, however, related to the polysulphides such as  $K_2S_4$ . **Potassium tetroxide** is a yellow powder which reacts with water to form potassium hydroxide and hydrogen peroxide, with evolution of oxygen.

**Ammonium peroxide**,  $(NH_4)_2O_2$ , is formed by the action of ethereal ammonia solution upon an ethereal solution of anhydrous hydrogen peroxide. It forms crystals at a low temperature of the composition  $(NH_4)_2O_2 \cdot H_2O_2$ , which break up at ordinary temperature into ammonia, water, and oxygen.



#### HALIDES

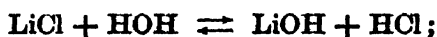
The following are the solubilities of the halides in water at about 15°:—

	Li	Na	K	Rb	Cs
F' ...	insol.	$\left\{ \begin{array}{l} 4 \\ NaHF_2 \text{ diff. sol.} \end{array} \right.$	$\left\{ \begin{array}{l} + 2H_2O \\ \text{very sol.} \\ KHF_2 \\ \text{easily sol.} \end{array} \right.$	?	?
Cl' ...	80	36	33.4	83	very sol.
Br' ...	150 (deliq.)	+ 2 H <sub>2</sub> O 87	63	104	?
I' ...	160 (deliq.)	+ 2 H <sub>2</sub> O 174	140	150	?

When these salts are anhydrous they crystallize in cubes. It may be observed first that the fluorides differ from the other halides in solubility; lithium fluoride, like the alkaline earth fluorides, is insoluble, and sodium fluoride is but slightly soluble in water; potassium fluoride contains water of crystallization, and sodium and potassium fluorides form the acid salts  $NaHF_2$  and  $KHF_2$ , which are derivatives of the double hydrofluoric acid molecule,  $H_2F_2$ . Many other examples of the exceptional properties of fluorides will be observed later. There is an increase in solubility in every known case in passing from the chlorides through bromides to iodides; it may also be observed in each case that a diminution in solu-

bility from the lithium through the sodium to the potassium halide is followed by a rise to the rubidium, and probably to the caesium salt. These variations in solubility serve to differentiate the "typical" elements lithium and sodium from potassium, rubidium, and caesium, which are placed at the head of three long periods, since a break in the sequence of solubilities occurs in each case at potassium.

The solubilities of the chlorides in alcohol follow the same order as their solubilities in water. Lithium, rubidium, and caesium chlorides, which are very soluble in water, also dissolve in alcohol; sodium and potassium chlorides, which are less soluble in water, are practically insoluble in alcohol. Sodium and potassium iodides, which are more soluble in water than the chlorides, are also somewhat soluble in alcohol. The resemblance between lithium and magnesium and calcium is shown in the extreme solubility of the halides, and in the fact that lithium chloride solution, when evaporated, undergoes hydrolysis in the sense of the equation



on account of the loss of hydrochloric acid and the solubility of lithium hydroxide, an aqueous solution of the residue obtained by evaporation to dryness is alkaline.

In contrast to the solubilities of the simple halides, the complex halides of the alkalis decrease in solubility from lithium to caesium. An example of this is seen in the case of the platinichlorides, whose solubilities in water are as follows:—

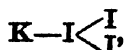
$\text{M}_2\text{PtCl}_6$	Li	Na	K	Rb	Cs
sol. at 10°.	easily sol.	easily sol.	0.90	0.154	0.05

The same diminution in solubility, with increase in basic properties of the metal, is observable with other complex salts. For instance, rubidium and caesium can be separated from potassium by reason of the slight solubility of the stannichlorides,  $\text{Rb}_2\text{SnCl}_6$  and  $\text{Cs}_2\text{SnCl}_6$ ; and caesium can be separated from rubidium by the precipitation of the antimonochloride,  $3 \text{CsCl}$ ,  $2 \text{SbCl}_3$ , the corresponding rubidium com-

pound being soluble in water. When it is considered that magnesium and the alkaline earth metals, together with lithium and sodium, do not form insoluble complex halides like those formed by potassium, rubidium, and caesium, it appears that the formation of such compounds is confined to the most electro-positive or basigenic of the elements only, the insolubility likewise increasing with increasing electro-positiveness.

Another characteristic of the alkali metals is the formation of polyhalides.

It is well known that iodine is more soluble in potassium-iodide solution than in water. This is due to the formation in solution of potassium tri-iodide  $KI_3$ , which may be isolated in the form of almost black, needle-shaped crystals. This compound is evidently not very stable, since the two atoms of iodine are removed again by the action of sodium thiosulphate. It is, however, a true "atomic" and not a "molecular" compound, since it has been shown that its solution contains the ions  $K^+$  and  $I_3^-$ . Its constitution may therefore be represented as

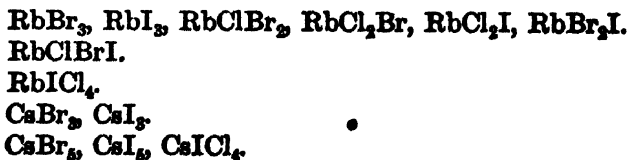


in which the potassium atom still remains monovalent.

The compounds  $LiICl_4$  and  $KICl_4$  are likewise known, in which the iodine atom may be supposed pentavalent.

In the case of rubidium and caesium a large number of these salts are known, which crystallize well and are more stable than the potassium salts.

The following are the best known:—



With salts containing more than one halogen element, since the ions into which they dissociate in solution are not known, the constitution must remain uncertain.

Some theoretical explanation of these remarkable compounds should be given; for unless the alkali metals are supposed to be polyvalent in them—and there is no reason to suppose this to be the case—the combination of the monohalide with free halogen is a phenomenon whose significance should be of interest.

It appears to be a function of the iodine ion to combine with free iodine, as in the solution of iodine in potassium iodide; but iodine in solution in an organic solvent such as nitrobenzene dissolves potassium iodide, which is insoluble in the pure solvent, this being due, as Dawson has shown,<sup>1</sup> to the formation of  $KI_3$  or  $KI_5$ , which does not separate  $K$  ions under such circumstances. It seems, therefore, that potassium iodide has a tendency to combine with iodine irrespective of the electrolytic dissociation of the salt; and that this tendency is more powerful with rubidium and caesium is shown by the stable polyhalides of these metals which exist. This tendency is therefore to be attributed to the intense electro-positiveness of the alkali metals, which thus have the power of conferring basic and polyvalent properties upon the halogen atom to which they are united.

Certain substituted ammonium derivatives furnish polyhalides which may be compared with the above. For instance, tetraethylammonium tri- and penta-iodide,  $(C_2H_5)_4NI_3$  and  $(C_2H_5)_4NI_5$ , are obtained by adding iodine solution to an aqueous solution of tetraethylammonium iodide. Ammonium tri-iodide itself has also been obtained; it is isomorphous with the tri-iodides of the alkali metals.

#### SULPHATES

The following are the solubilities in 100 parts of water at 18° of the anhydrous sulphates of the alkali metals:—

$Li_2SO_4$	$Na_2SO_4$	$K_2SO_4$	$Rb_2SO_4$	$Cs_2SO_4$
34.6	16.9	10.7	about 44.	about 163.

The order of solubility is the same as in the case of the chlorides, differentiation between metals in the typical and

<sup>1</sup> *Chem. Soc. Trans.* LXXIV. (1904), 467.



in the long periods being shown. Lithium sulphate often crystallizes with 1  $\text{H}_2\text{O}$  and sodium sulphate with 7 or 10  $\text{H}_2\text{O}$ ; the other sulphates are anhydrous. Acid sulphates,  $\text{MHSO}_4$ , are known in each case, that of lithium being the least stable.

It was observed in the case of the chlorides that double or complex salts show an order of solubility which is the reverse of that of the simple salts; the same is true of the double sulphates known as alums,  $\text{M}'_2\text{SO}_4, \text{R}'''_2(\text{SO}_4)_3, 24 \text{H}_2\text{O}$ , which show an increase in stability and insolubility with increase in basigenic properties of the alkali metal. Lithium sulphate probably does not form an alum; sodium alum is very soluble in water and difficult to obtain in a pure, crystalline condition; potassium alum is well known; rubidium alum is much less soluble than the potassium compound, and nearly four times as soluble as caesium alum. The following are the solubilities at  $17^\circ$ :—

Na-	K-	Rb-	Cs-	Alum
about 51	13.5	2.27	0.619	

The solubility of ammonium alum is 13.7 at  $20^\circ$ .

The stability of alums, as well as of other double and complex salts, undoubtedly depends upon the magnitude of the difference of basigenic property between the metals of the constituent simple salts; and this is illustrated in the alums by the increase of stability from lithium to caesium. A distinction is generally drawn between double and complex salts in the sense that whilst the former are decomposed into their constituent simple salts in solution, the latter preserve their identity in solution, giving rise to complex ions. The alums and other double sulphates, such as  $\text{K}_2\text{SO}_4, \text{MgSO}_4, 6 \text{H}_2\text{O}$ , are then considered to belong to the class of double salts which break up in solution, whilst the platinichlorides and ferro- and ferricyanides are complex salts, yielding complex ions in solution. This distinction, however, is an artificial one. It has been shown that in concentrated solutions of the double sulphates such as the alums complex ions exist, which

are dissociated on dilution; whilst in dilute solutions of complex salts, such as ferrocyanides, simple ions, such as the cyanogen ion (CN)', are present in small amount. The difference, therefore, between double and complex salts is in degree rather than kind.

#### CARBONATES, NITRATES, PHOSPHATES, AND SULPHIDES

The solubilities of the carbonates and bicarbonates in water and alcohol are given in the following table, as far as data are available:—

	Li	Na	K	Rb	Cs
$M_2CO_3$ in water .... {	1.33	21.4	112	very sol.	very sol.
	(at 20°)	(at 20°)	(at 20°)	and deliq.	and deliq.
$M'HCO_3$ in water... {	5.5	9.84	26.9	sol. not	sol. not
	(at 13°)	(at 20°)	(at 20°)	deliq.	deliq.
$M_2CO_3$ in alcohol at {	insol.	insol.	?	0.74	11.1
atm. temp. .... }					

It is instructive to observe that lithium resembles the alkaline earth metals, not only in the slight solubility of its carbonate in water, but also by the fact that its bicarbonate is more soluble than its carbonate, which is the reverse of what obtains with the other alkali metals.

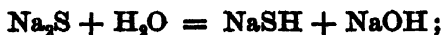
The nitrates and phosphates of the alkalis need but brief mention in a comparative treatment.

Lithium and sodium nitrates are very soluble in water, potassium and rubidium nitrates rather less, and caesium nitrate sparingly soluble. Lithium and sodium nitrates are isomorphous; potassium nitrate is dimorphous, one of its forms being isomorphous with the foregoing; rubidium and caesium nitrates combine with nitric acid, forming acid nitrates.

Lithium phosphate is nearly insoluble in water, like the alkaline earth phosphates; sodium and potassium phosphates show little resemblance to one another; there is no potassium compound, for instance, corresponding to the well-known sodium salt  $Na_2HPO_4 \cdot 12 H_2O$ .

Sulphides are obtained in the dry way by the reduction of sulphates by heating with charcoal, or by fusion of sulphur

with alkali carbonate. These products, however, contain polysulphides and thiosulphates.<sup>1</sup> When alkali hydroxide solution is saturated with hydrogen sulphide, hydrosulphide is formed, and in the case of potassium the crystallized compound  $2 \text{KSH} \cdot \text{H}_2\text{O}$  may be obtained from the solution. By the addition of an equivalent of alkali the normal sulphide is produced, the crystalline salts  $\text{Na}_2\text{S} \cdot 9 \text{H}_2\text{O}$  and  $\text{K}_2\text{S} \cdot 5 \text{H}_2\text{O}$  having been isolated. These compounds, when dissolved in water, yield alkaline solutions owing to hydrolysis, for example:—



and quickly undergo atmospheric oxidation, the first result being the liberation of sulphur which by combination with sulphide forms yellow polysulphides, this being followed by further oxidation to thiosulphate, the solution again becoming colourless.

Colourless ammonium hydrosulphide solution turns yellow from the same cause; in this case, owing to loss of ammonia, sulphur and water eventually remain.

### SUMMARY

Many of the facts brought forward in the above study of the salts of the alkali metals reveal a gradation of properties in accordance with the increase in atomic weight from member to member, as well as a modification in properties in passing from the typical elements lithium and sodium to the members of the long periods, potassium, rubidium, and caesium.

Tutton has shown, in a series of recent researches, that the morphological and physical properties of the crystals of the various salts of potassium, rubidium, and caesium—such properties as solubility in water, molecular volume, refractive indices, and general optical properties—follow the order of progression of the atomic weights of these metals.

The position of ammonium in the series of the alkali metals

<sup>1</sup> Liver of sulphur or "potassa sulphurata", formed by heating sulphur with potassium carbonate, is of variable composition, but contains polysulphides, sulphate and thiosulphate.

may be remarked upon. It is well known that the salts of the radicle ( $\text{NH}_4$ ) are analogous to the salts of the alkalis as regards isomorphism and solubility. Tutton has recently shown<sup>1</sup> that the properties of ammonium salts are closely related to those of rubidium compounds, and that ammonium stands between rubidium and caesium in the series of the alkali metals. The following relative values for the molecular volumes of the sulphates illustrate this statement:—

	Mol. Vol.
Potassium sulphate.....	65.33
Rubidium „ .....	73.77
Ammonium „ .....	74.63
Cæsium „ .....	85.17

It is remarkable that the molecules of ammonium sulphate occupy almost the same volume as those of the rubidium salt, although they contain eight more atoms. Two alternative views of molecular structure may be put forward to explain this circumstance: either that the space within the molecule of an alkali sulphate is so sparsely occupied that the additional atoms of the ammonium salt can be accommodated without molecular enlargement, or else that the molecular interspaces, even in the solid state, are so large compared with the size of the molecules themselves, that enlargement consequent upon the presence of additional atoms within the molecule has no influence upon the number of molecules within a given volume.

#### COPPER, SILVER, AND GOLD

It was stated in the introduction to this group that these three metals which form sub-group I B are related on the one hand to nickel, palladium, and platinum, and on the other to zinc, cadmium, and mercury. This is shown in the following table:—

Ni (58.68)	Cu (63.57)	Zn (65.37)
Pd (106.7)	Ag (107.88)	Cd (112.40)
Pt (195.2)	Au (197.2)	Hg (200.0)

<sup>1</sup> *Chem. Soc. Trans.* lxxxiii. (1908), 1049.

This is an illustration of the rule that the properties of an element are the mean of those of its atomic analogues, that is, of adjacent elements in series and in group; thus the atomic analogues of silver are palladium, cadmium, copper, and gold, or, more strictly, the unknown element represented by the blank space between silver and gold.

In the study, therefore, of the elements copper, silver, and gold, the relationships thus suggested may be looked for, as well as slight similarities to the alkali metals which are the analogous members of sub-group I A.

The densities, atomic volumes, and melting-points of the elements are as follows:—

	Cu	Ag	Au
Dens.....	8.93	10.49	19.265
At. Vol.....	7.12	10.29	10.23
M.P.....	1085°	960.5°	1062°

It is thus observed that the atomic volumes are relatively small, the elements occurring near the minima of the atomic-volume curve; and whilst it was found that the possession of large atomic volume in the case of the alkali metals is associated with great chemical activity and affinity for oxygen, the contrary property possessed by copper, silver, and gold is connected with comparative inertness and weak power of combination with oxygen. Moreover, the affinity for oxygen is found to diminish with rising atomic weight from copper to gold, as well as from nickel to platinum, and from zinc to mercury. A gradation is observable in the reducibility of copper, silver, and gold solutions, for whilst cuprous oxide is precipitated from alkaline cupric solutions by glucose, the metals are precipitated from silver and gold solutions by this reagent; and ferrous sulphate precipitates gold, and less readily silver, but not copper from solution. As was pointed out in Chap. II, this diminution in chemical activity with rise of atomic weight, which is confined to the elements of Groups VIII, I B and II B, is associated with a diminution in electro-positiveness according to the electro-potential series.

As regards the melting-points of these metals, it may be

observed that whilst the figures do not show a gradation among themselves, the metals form a link between the high melting members of the eighth group and the fusible metals of Group II B. For instance, nickel melts above  $1400^{\circ}$ , and zinc at  $433^{\circ}$ , whilst the melting-point of copper lies about midway between these two. Each of these metals may be obtained, like platinum, in a colloidal form, apparently soluble<sup>1</sup> in water, by forming the electric arc between terminals of the metal under water, and also by reducing their salt solutions by suitable reagents. The difference between the colloidal and ordinary forms is clearest in the case of silver; solid, allotropic, variously coloured modifications, which do not conduct the electric current, being obtainable.

The physical properties of these elements, as well as their chemical properties, as manifested by their comparative stability towards air, water, and some acids, show them to be analogous to the members of the eighth group, with which they are sometimes classed. Nevertheless, as will be seen, some relationship with the alkali metals is maintained, especially in the compounds of lower valency.

#### OXIDES OF THE TYPE $M_2O$ AND THEIR SALTS

Cuprous oxide,  $Cu_2O$ , silver oxide,  $Ag_2O$ , and aurous oxide,  $Au_2O$ , stand in the order of decreasing stability. Cuprous oxide is the most stable oxide of copper at high temperature, being formed by heating copper or cupric oxide to a white heat in air; silver oxide loses its oxygen between  $250^{\circ}$  and  $300^{\circ}$ ; and aurous oxide at  $250^{\circ}$ . The stability of the hydroxides follows the same order. Cuprous hydroxide,  $Cu_2(OH)_2$ , is precipitated as a yellow powder, which easily loses water, when alkali-hydroxide solution is added to a cuprous salt, the oxide, however, being formed when an alkaline cupric solution is reduced by glucose or an arsenite.

Silver oxide, precipitated as a chocolate-coloured powder from a silver salt by an alkali, is somewhat hydrated and

<sup>1</sup> See note, p. 148 (Group III).

slightly soluble in water, giving an alkaline reaction, but the hydroxide cannot be said definitely to exist.

Aurous hydroxide is unknown, but the violet powder formed by adding alkali to a solution of an aurous salt forms a violet liquid with water in which aurous oxide is contained in colloidal suspension. Cuprous and silver oxides, when precipitated by dilute ammonia, dissolve in excess of the reagent, forming hydroxides of the basic radicles  $[M(NH_3)]$  or  $[M(NH_3)_2]$ . When a solution of silver oxide in ammonia is evaporated by exposure to the air, or when alcohol is added to the solution, silver nitride, known as fulminating silver on account of its explosive properties, is precipitated.

**Halides.**—Although the salts  $Cu_2Cl_2$ ,  $AgCl$ , and  $AuCl$  are insoluble in water, the first two at least may be obtained crystallized in cubes isomorphous with the chlorides of the alkalis. Cuprous chloride is volatile, and its vapour density corresponds to the molecular formula  $Cu_2Cl_2$ ; in dilute quinoline solution, however, the molecule is  $CuCl$ .<sup>1</sup> The molecular formulæ of silver and aurous chlorides are unknown, but the metals are considered to be monovalent in these compounds.

Cuprous chloride is hydrolysed by excess of water, according to the reaction



silver chloride is stable towards water, dilute acids, and alkalis; but aurous chloride is decomposed by warm water thus:—



the lower chlorides of indium undergo a similar reaction, as well as some mercurous compounds.

All these monochlorides form unstable double salts with alkali chlorides; cuprous chloride dissolves in hydrochloric acid, probably forming the compound  $H_4Cu_2Cl_6$ , to which the salt  $K_4Cu_2Cl_6$  corresponds. A solution of cuprous chloride in hydrochloric acid absorbs carbon monoxide, the compound  $CO \begin{smallmatrix} \text{CuCl} \\ \text{CuCl} \end{smallmatrix}$  resulting. The slight solubility of silver chloride

<sup>1</sup> Beckmann, *Zeit. Anorg. Chem.* (1906), 51, 226.

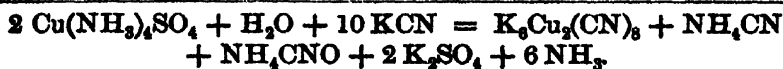
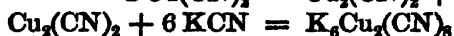
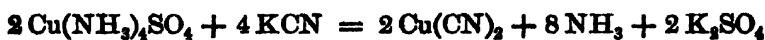
in water is perceptibly increased by the addition of hydrochloric acid. Cuprous and silver bromides and iodides are similar to the chlorides. All these halides dissolve in aqueous ammonia, forming amines containing basic ions such as  $[\text{CuNH}_3]'$  and  $[\text{Ag}(\text{NH}_3)_2]'$ . In the case of silver there is progressive insolubility from the chloride to the iodide. Silver halides also dissolve in sodium thiosulphate solution, forming the complex salt  $\text{Na}_4[\text{Ag}_2(\text{S}_2\text{O}_3)_3]$ .

**Complex Cyanides** are known in the case of cuprous, silver, and aurous compounds. Cuprous cyanide dissolves in potassium-cyanide solution according to the following reaction:—



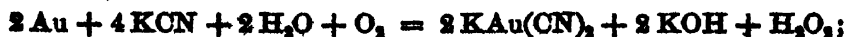
the potassium cuprocyanide produced being sufficiently stable to resist decomposition by hydrogen sulphide in neutral or alkaline solution. The well-known analytical separation of copper and cadmium depends on this fact, since the cadmium double cyanide,  $\text{K}_2\text{Cd}(\text{CN})_4$ , is decomposed by hydrogen sulphide.

The reaction is generally carried out by the addition of potassium cyanide to cuprammonium-sulphate solution, when the following changes take place:—



Silver cyanide unites with potassium cyanide to form  $\text{KAg}(\text{CN})_2$ , which may be obtained solid, but is decomposed by hydrogen sulphide.

Potassium aurocyanide, which may be obtained in crystals, is formed when finely-divided gold dissolves in potassium-cyanide solution in presence of air. The following reaction takes place:—





the  $\text{H}_2\text{O}_2$  produced reacting with more gold thus:—



These reactions form the basis of the cyanide gold process, the metal being obtained by electrolysis of the solution, or precipitation by zinc.

The three oxides of the type  $\text{M}'_2\text{O}$  differ considerably in their power of forming **oxysalts**.

The only oxysalts corresponding to  $\text{Cu}_2\text{O}$  at present known are cuprous sulphite, thiosulphate, and sulphate; the two former of these form double salts with the corresponding alkali compounds. When cuprous oxide is acted on by dilute nitric or sulphuric acid, a solution of cupric salt is obtained, together with metallic copper. Thus, for instance:—



By bringing together cuprous oxide and methyl sulphate, however, in the absence of water, Recoura<sup>1</sup> obtained cuprous sulphate as a grey powder, which is immediately decomposed by water into cupric sulphate and copper.

Oxysalts corresponding to  $\text{Ag}_2\text{O}$ , such as the nitrate and sulphate, are well known, and seem to take the place of the unknown salts of the oxide  $\text{AgO}$ . Except the carbonate  $\text{Ag}_2\text{CO}_3$ , they do not appear to be hydrolysed by water.

Aurous oxide,  $\text{Au}_2\text{O}$ , resembles cuprous oxide in its slight power of salt formation; the sulphite and thiosulphate are known, but the common oxysalts do not appear to exist.

Viewed from the standard of the periodic law, these three oxides present certain anomalies. Silver oxide evidently does not belong to the same category as cuprous and aurous oxides, and as regards these two oxides the former is probably the more basic, just as copper is more electro-positive than gold.

#### CUPRIC AND AURIC OXIDES\* AND THEIR SALTS

**Cupric oxide**,  $\text{CuO}$ , and its salts are well known, and require but brief treatment.  $\text{Cu}(\text{OH})_2$  precipitated as a blue solid when alkali hydroxide solution is added to a cupric salt, dis-

<sup>1</sup> *C. r. de l'Acad. des Sciences*, 148, 1106-8.

solves in excess of concentrated alkali, forming a blue solution. The acidic property of cupric hydroxide thus shown is further illustrated by the tenacious way in which alkali is retained by the dark-brown, somewhat hydrated, cupric oxide obtained by boiling the hydroxide with water.

Cupric salts usually contain water of crystallization, and are then blue or green, being white or yellow when anhydrous. Of the halides, the iodide is unstable, breaking down, on formation, into cuprous iodide and iodine. The nitrate is decomposed on heating, leaving the oxide, thus resembling the nitrates of heavy metals, and differing from the nitrates of the members of the alkali group. The carbonate and phosphate are insoluble in water, the former always being basic; the compound  $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$  is well known in the mineral malachite. The sulphate also forms basic salts, its dilute aqueous solution being hydrolysed by boiling, with the formation of sulphuric acid and an insoluble green basic sulphate. Basic salts are also formed when the normal sulphate is kept for several hours at a dark-red heat, as well as by fractional precipitation with alkali-hydroxide solution.

Cupric sulphate forms isomorphous mixtures with the sulphates of the metals adjacent to copper in the periodic table, that is, with zinc sulphate and the sulphates of iron, nickel, and cobalt; this notwithstanding the fact that cupric sulphate normally crystallizes with five molecules of water and all the other sulphates with seven. Whether or not the mixed crystals contain five or seven molecules of water depends on the proportion of cupric sulphate present.

Cupric sulphate forms double salts with the sulphates of the alkali metals, that with ammonium sulphate,  $\text{CuSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , being the best known. In these salts a molecule of alkali sulphate takes the place of one of water in the heptahydrated salt. These salts are isomorphous with the corresponding double salts containing ferrous iron, nickel, cobalt, zinc, and magnesium.

The blue solution obtained by adding excess of ammonia to cupric sulphate solution contains the compound  $[\text{Cu}(\text{NH}_3)_4]^{2+}$

$\text{SO}_4$ . Further reference will be made to this compound at the end of chapter XII.

**Auric oxide** is represented by the formula  $\text{Au}_2\text{O}_3$ , and its chloride is  $\text{AuCl}_3$ . Compounds of the empirical formulæ  $\text{AuO}$  and  $\text{AuCl}_2$  are known, but they must be considered as aurous aurate,  $\text{Au} \cdot \text{AuO}_2$ , and chloraurate,  $\text{Au} \cdot \text{AuCl}_4$ , respectively. The existence of a sesquioxide, and compounds corresponding thereto, confers upon gold in the auric compounds more pronounced acidic properties than have hitherto appeared in this group.

Auric hydroxide,  $\text{Au}(\text{OH})_3$ , is precipitated as a brown powder when potassium hydroxide is added to a concentrated solution of auric chloride; it is soluble in excess of alkali, forming aurate,  $\text{KAuO}_2$ , from which it is again precipitated by dilute nitric acid. When dehydrated,  $\text{Au}(\text{OH})_3$  first forms auryl hydroxide,  $\text{AuO} \cdot \text{OH}$ , and then auric oxide,  $\text{Au}_2\text{O}_3$ , which decomposes below  $250^\circ$  into its elements.

The aurates, for instance  $\text{KAuO}_2 \cdot 3\text{H}_2\text{O}$ , are well-defined crystalline salts, soluble in water, and yielding alkaline solutions which are rather unstable. Auric oxide is almost exclusively acidic in function, and forms no stable oxysalts. It is thus less basic than alumina, which forms a fairly stable sulphate.

When concentrated ammonia is added to auric oxide a substance of the empirical composition  $\text{AuN}_2\text{H}_3 \cdot 3\text{H}_2\text{O}$ , known as fulminating gold, is produced. This compound is generally assumed to be  $\text{Au} \left\langle \begin{smallmatrix} \text{NH} \\ \text{NH}_2 \end{smallmatrix} \right\rangle \cdot 3\text{H}_2\text{O}$ , but is possibly an ammine of the composition  $\left[ \text{Au} \left\{ \begin{smallmatrix} (\text{NH}_3)_2 \\ (\text{OH})_2 \end{smallmatrix} \right\} \right] \text{OH}$ .

The trihalides of gold present many of the properties of halanhydrides, whilst their saline qualities are very feeble. Auric chloride,  $\text{AuCl}_3$ , obtained by carefully evaporating a solution of gold in chlorine water, is a brown crystalline mass, soluble in alcohol and ether, and melting at  $288^\circ$ . Orange-red crystals,  $\text{AuCl}_3 \cdot 2\text{H}_2\text{O}$ , may be obtained from aqueous solution; it also forms chlorauric or aurichloric acid,  $\text{HAuCl}_4$ ,

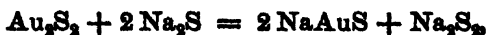
$3\text{H}_2\text{O}$ , with hydrochloric acid, from which chloraurates or aurichlorides, such as  $2\text{KAuCl}_4$ ,  $\text{H}_2\text{O}$  are derived. Auric chloride thus resembles platinic chloride in combining with alkali chlorides to form complex alkali salts.

Auricyanides are well known, potassium auricyanide,  $\text{KAu}(\text{CN})_4$ , being obtained by adding concentrated potassium-cyanide solution to a neutral solution of auric chloride. It is a colourless salt, from which white crystals of the acid  $\text{HAu}(\text{CN})_4$  can be obtained.

#### SULPHIDES

Copper forms two sulphides,  $\text{Cu}_2\text{S}$  and  $\text{CuS}$ , corresponding to cuprous and cupric oxides; cupric sulphide loses sulphur when heated gently out of contact with air, yielding cuprous sulphide, which is also produced when the metal is heated with sulphur. Both compounds occur in nature, though cuprous sulphide, like the oxide, is more stable than the corresponding cupric compound. Cupric sulphide shows very feebly acidic properties, being perceptibly soluble in alkali-sulphide solutions.

Silver forms but one sulphide,  $\text{Ag}_2\text{S}$ , a black solid insoluble in water, alkalis, and alkali sulphides. Three sulphides of gold are known,  $\text{Au}_2\text{S}$ ,  $\text{Au}_2\text{S}_2$ , and  $\text{Au}_2\text{S}_3$ , the latter of which is very unstable. Aurous sulphide,  $\text{Au}_2\text{S}$ , formed by reducing a hot solution of auric chloride with hydrogen sulphide, combines with alkali sulphides, forming thioaurites,  $\text{MAuS}$ . The disulphide,  $\text{Au}_2\text{S}_2$ , possibly aurous thioaurate,  $\text{AuAuS}_2$ , is formed when hydrogen sulphide acts upon cold auric-chloride solution. It reacts with sodium sulphide, thus:—



and combines with a polysulphide, forming thioaurate. Auric sulphide,  $\text{Au}_2\text{S}_3$ , which is thioauric anhydride, combining with alkali sulphides to form thioaurates, is not formed in the wet way, but by passing hydrogen sulphide over a heated aurichloride.

The superior acidic properties of gold as compared with

silver and copper compounds are well illustrated in the properties of the above sulphides.

#### SUB- AND PER- OXIDES

**Copper quadrantoxide**,  $\text{Cu}_4\text{O}$ , is formed as an olive-green powder by the reduction of an alkaline cupric solution by stannous chloride. The copper first passes through the cuprous stage, and finally separates as metal if reduction is continued. This oxide forms no salts, but is decomposed by acids as follows:—



**Silver quadrantoxide**,  $\text{Ag}_4\text{O}$ , possibly exists, and the subhalides  $\text{Ag}_4\text{F}_2$  and  $\text{Ag}_4\text{Cl}_2$  are known, the latter being produced by the decomposition of  $\text{AgCl}$  by light.

**Copper peroxide**,  $\text{CuO}_2$ ,  $\text{H}_2\text{O}$ , is formed as a yellowish-brown crystalline powder by the action of dilute hydrogen peroxide on cupric hydroxide; it is unstable when moist,

and is probably a superoxide having the constitution  $\text{Cu} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array}$

since with dilute acids it gives cupric salts and hydrogen peroxide.

**Silver peroxide**,  $\text{AgO}$ . When a neutral solution of silver nitrate undergoes electrolysis, a black powder is deposited at the anode, which is a peroxide of silver,  $\text{Ag}_2\text{O}_4$ . When this compound is boiled with water oxygen is evolved, and the oxide  $\text{AgO}$  remains. This latter oxide does not decompose hydrogen peroxide, and therefore is not a superoxide. There is reason to believe that it is a feebly basic oxide, and the analogue of cupric oxide,  $\text{CuO}$ ; but in chemical properties it is similar to lead peroxide,  $\text{PbO}_2$ .

## CHAPTER VI

## GROUP II

SUB-GROUP A		SUB-GROUP B
	Be (9.1)	
	Mg (24.32)	
Ca (40.09)		Zn (65.37)
Sr (87.63)		Cd (112.40)
Ba (137.37)		•
		Hg (200.0)
Ra (226.4)		

The metals calcium, strontium, and barium of sub-group A, immediately following potassium, rubidium, and caesium, respectively, in series, form a group of closely-allied electro-positive elements, the metals of the alkaline earths; to which must be added, after a blank space in the group, the newly-discovered element radium. The metals of this group are less electro-positive than their neighbours of Group I.

Sub-group B, containing the metals zinc, cadmium, and mercury, is related to sub-group A in the same general manner as is I B to I A. Its members are less positive than the metals of the alkaline earths, and, as might be anticipated from the relative positions of the two sections of the group in the long series, they do not present any striking resemblances to the alkaline-earth metals. The group valency, two, is, however, characteristic.

Beryllium and magnesium are more similar in their properties to zinc than to the alkaline-earth metals, and might therefore be placed in Group II B.

In some respects, however, these two elements, and magnesium in particular, may be regarded as linking the alkaline-earth to the zinc group; and they will, therefore, be dealt with first as the "typical" elements of the group.

## BERYLLIUM (GLUCINUM) AND MAGNESIUM

From their positions in series, beryllium between lithium and boron, and magnesium between sodium and aluminium, it is evident that magnesium should be more electro-positive

or basigenic than beryllium. That this is the case is shown by the following facts:—

Beryllium hydroxide is feebly acidic, being dissolved by cold alkali hydroxides, whilst magnesium hydroxide is not so dissolved. Metallic beryllium does not combine with oxygen so readily as magnesium, nor does it so readily decompose water; moreover, it may be obtained by reducing the oxide with magnesium. Beryllium yields basic salts more readily than magnesium.

Both these metals<sup>1</sup> can be prepared from their chlorides by reduction with sodium or potassium, or by electrolysis. Both metals have a silvery lustre and low density; that of beryllium is 1.64, and of magnesium 1.75, the atomic volumes being 5.55 and 13.90. Neither metal is easily oxidized or acted on by water; boiling water, indeed, slowly reacts with magnesium, but not with beryllium. Magnesium melts at 800° and beryllium somewhat higher. These metals are easily dissolved by dilute hydrochloric and sulphuric acids, and magnesium by nitric acid; but beryllium is scarcely acted on by nitric acid, in this resembling aluminium. Beryllium also resembles aluminium, and differs from magnesium, in being soluble in alkali hydroxides.

In the properties of the element and its compounds beryllium bears a relationship to the alkaline-earth metals similar to that which lithium bears to the alkalis; and the relationship of beryllium in the second group to aluminium in the third is paralleled by that of boron in the third group to silicon in the fourth.

The oxides  $\text{BeO}$  and  $\text{MgO}$  are both formed by the ignition of the metals in air, as well as of oxy-salts, such as the nitrates, carbonates, and sulphates, in presence of water vapour. Beryllium sulphate is, however, much more easily decomposed than magnesium sulphate, as becomes the inferior electro-positive

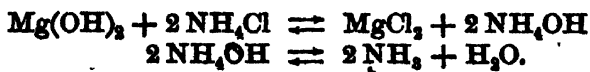
<sup>1</sup> Beryllium is rather scarce; beryl,  $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ , is the chief mineral. The occurrence of magnesium as sulphate in Epsom-salt,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , as chloride in carnallite,  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , as carbonate in magnesite,  $\text{MgCO}_3$ , and dolomite,  $(\text{MgCa})\text{CO}_3$ , as well as in many silicates, recalls the manner of occurrence of the alkaline-earth metals.

character of the former metal. A comparison of the ease of decomposition of these oxysalts with those of the alkali and alkaline-earth metals is instructive, for the sulphates of the alkaline-earth metals are not decomposed at a red heat, nor are the carbonates of the alkalis so decomposed, whilst their nitrates, on powerful ignition, lose only oxygen, forming nitrite. After powerful ignition beryllium oxide is insoluble in acids, thus resembling aluminium oxide; magnesium oxide is not thus rendered insoluble.

The oxides of beryllium and magnesium are both produced by the gentle ignition of their hydroxides, and are not again completely converted into hydroxides by the action of water. Magnesium oxide, however, is sufficiently soluble in water to give an alkaline reaction, the solution containing magnesium hydroxide.

Magnesium hydroxide is soluble in ammonium-chloride solution, and this property finds an application in chemical analysis, ammonium chloride preventing the precipitation of magnesium hydroxide by ammonia. This fact is explained on the ionic theory by the formation of ammonium hydroxide by interaction of ammonium chloride with the small amount of magnesium hydroxide in solution in water; this ammonium hydroxide is only slightly dissociated into ammonium and hydroxyl ions in solution, and some of it decomposes into ammonia and water. Thus the concentration of OH ions in solution is diminished, and more  $\text{Mg}(\text{OH})_2$  dissolves in consequence.

The following equations illustrate these reactions:—



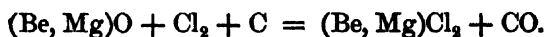
At the same time the double or complex salt  $(\text{NH}_4)_2\text{MgCl}_4$  is probably formed in solution, and the presence of magnesium in the ion  $\text{MgCl}_4$  would prevent its precipitation by ammonium hydroxide.

As has already been stated,  $\text{Be}(\text{OH})_2$  dissolves in cold alkali-hydroxide solutions, forming the compounds  $\text{Be}(\text{OM})_2$ . From



these solutions a polymeric form of hydroxide separates on boiling or long standing in the cold. In this property beryllium hydroxide differs from zinc and aluminium hydroxides, but resembles chromic hydroxide. Magnesium hydroxide is not soluble in alkalis.

The chlorides  $\text{BeCl}_2$  and  $\text{MgCl}_2$  both result from the action of hydrochloric acid on the metals or oxides. They are formed in the anhydrous state by the action of chlorine on a heated mixture of the oxides with carbon:



$\text{BeCl}_2$  crystallizes in silky needles which melt at about  $600^\circ$  and sublime at a somewhat higher temperature;<sup>1</sup>  $\text{MgCl}_2$  crystallizes in pearly leaflets, which can be melted and distilled at a red heat in an atmosphere of hydrogen.

Both salts are deliquescent, and crystallize in the hydrated forms  $\text{BeCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  respectively. The hydrated salts readily yield basic compounds on warming, and many such basic salts of beryllium of doubtful composition have been described.

When hydrated magnesium chloride is decomposed by heat the oxychloride  $\text{Mg} \begin{smallmatrix} \text{OH} \\ \text{Cl} \end{smallmatrix}$  is formed, whilst the anhydrous chloride, when heated in moist air, yields the oxide and chlorine,



a reaction which is employed technically in the Weldon-Pechiney chlorine-recovery process. Beryllium chloride behaves similarly. Magnesium chloride forms stable double salts with the alkali chlorides of the type  $\text{MCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ .<sup>2</sup>

**Other Salts.** Of the other salts of these metals reference may be made to the carbonates and sulphates.

**Beryllium carbonate** separates in the hydrated crystalline

<sup>1</sup>  $\text{BeCl}_2$ , obtained from beryl, appears to be variable in composition, a fact which points to the possible presence of an unknown element in this mineral.

—Pollok, *Chem. Soc. Trans.*, lxxv. (1904), 1680.

<sup>2</sup> The mineral carnallite is  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ .

form,  $\text{BeCO}_3, 4 \text{H}_2\text{O}$ , from the solution obtained by passing carbon dioxide through water containing the hydroxide in suspension. This solution probably contains bicarbonate. The normal salt very easily gives off carbon dioxide, forming basic carbonate.

**Magnesium carbonate** is isodimorphous with calcium carbonate; it occurs as the mineral magnesite. It may be obtained in the hydrated condition,  $\text{MgCO}_3, 3 \text{H}_2\text{O}$ , in the same way as beryllium carbonate. It is hydrolysed by much water, a basic carbonate being precipitated. Hydrated basic carbonates are also obtained by precipitating solutions of magnesium salts with sodium carbonate solution. These vary in composition according to the circumstances of their formation. The *magnesia alba* of commerce is supposed to be  $3 \text{MgCO}_3, \text{Mg}(\text{OH})_2$  together with some water. The compound  $4 \text{MgCO}_3, \text{Mg}(\text{OH})_2, 4 \text{H}_2\text{O}$  is also well known. It may be supposed that in the precipitation of a basic carbonate the normal carbonate is first formed and then hydrolysed by water, the insolubility of the hydroxide accounting for its presence in the precipitate. Such a reaction is very characteristic of compounds of the less distinctly basigenic metals, salts of weak acids showing a greater tendency to be hydrolysed than those of stronger acids. No carbonate, indeed, is known whose aqueous solution is neutral in reaction; the carbonates of the alkalis are shown to have undergone incipient hydrolysis in solution by their alkaline reaction, this phenomenon being accounted for by the presence of  $\text{OH}$  ions derived from alkali hydroxide.

The metals zinc, mercury, lead, and copper are analogous to magnesium in the readiness with which they form basic carbonates. It is interesting to observe that in the case of still less basigenic elements, such as ferric iron and aluminium, the action of alkali carbonates in solution leads to the production of hydroxides only; that is, the carbonates are completely hydrolysed by water. Sulphides are similar to carbonates in their instability, since hydrogen sulphide is an acid comparable in strength with carbonic acid. Thus magnesium,

aluminium, chromic, and other sulphides are unstable towards water, being hydrolysed with the production of metallic hydroxide and hydrogen sulphide.

**Beryllium sulphate**,  $\text{BeSO}_4$ , generally crystallizes with four molecules of water; a heptahydrated salt is however known which is isomorphous with magnesium sulphate. This compound easily gives rise to basic salts, a number of which are known. The tendency to hydrolysis is shown by the acid reaction of the aqueous solution of the salt. When ignited strongly, crystallized beryllium sulphate loses water and sulphur trioxide, leaving a residue of the pure oxide. This reaction has been employed in determining the atomic weight of beryllium.

**Magnesium sulphate** usually crystallizes in rhombic prisms containing  $7 \text{ H}_2\text{O}$ , and isomorphous with zinc sulphate. It is known, however, in other forms containing amounts of water varying from 1 to  $24 \text{ H}_2\text{O}$ . The heptahydrated form can exchange one of its molecules of water for a molecule of an alkali sulphate; double salts, such as  $\text{MgSO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $6 \text{ H}_2\text{O}$ , being formed. In this it resembles zinc sulphate. No basic sulphate is known.

The sulphates of beryllium and magnesium, though less stable than those of the alkaline-earth metals, and therefore less perfect salts, differ from these by their ready solubility in water.

Beryllium forms no superoxide of the type  $\text{M} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array}$ , but magnesium forms an unstable compound of  $\text{MgO}$  and  $\text{MgO}_2$ , which is decomposed below  $40^\circ$ .<sup>1</sup>

Magnesium forms a nitride,  $\text{Mg}_3\text{N}_2$ , by direct union, when the metal is heated in nitrogen gas. This is decomposed by strong ignition in air or oxygen, and is acted upon by water, thus:—



Lithium, which resembles magnesium in some respects, as would be expected from the periodic law, forms a similar compound.

<sup>1</sup> Buff and Geissel Ber. 1904, xxxvii. 3683.

## CALCIUM, STRONTIUM, AND BARIUM

These elements display great similarity to one another in modes of occurrence<sup>1</sup> and properties. Reduction of the halides by sodium or potassium, or electrolysis of halides, are methods available for the isolation of the metals. Metallic calcium has lately been obtained in quantity<sup>2</sup> by the electrolysis of fused calcium chloride, an iron cathode being employed which just touches the surface of the chloride, and which is slightly raised at intervals so that the film of molten calcium upon it may solidify. Thus a rod of metal is gradually built up which contains 97 per cent of calcium, and which shows a white metallic surface when cut. Moissan has determined the density of calcium to be 1.548<sup>3</sup> and its melting-point 810°.

These metals possess higher melting-points than the alkali metals, and are less easily oxidized. They are comparatively stable in the air, but combine with oxygen and the halogens when heated with them. They decompose water with evolution of hydrogen at atmospheric temperature, though less vigorously than the alkali metals. Their chlorides are volatile in, and colour the Bunsen flame, giving spectra which are more complex than those of the alkali metals. The spectra of the metals themselves differ slightly from those of their chlorides. The chemical activity of calcium is comparable with that of lithium, and the activity increases with increasing atomic weight through strontium to barium.

The hydroxides, carbonates, and nitrates of these metals are more easily decomposed by heat than the corresponding compounds of the alkali metals, and, moreover, in the case of calcium, the chloride tends to form basic salts, that is, it is relatively easily hydrolysed. This is all in accordance with the position of these elements in the periodic system.

<sup>1</sup> In addition to the minerals calcite  $\text{CaCO}_3$ , strontianite  $\text{SrCO}_3$ , witherite  $\text{BaCO}_3$ , anhydrite  $\text{CaSO}_4$ , and gypsum  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , celestine  $\text{SrSO}_4$ , heavy-spar  $\text{BaSO}_4$ , isomorphous mixtures or compounds occur in barytocalcite  $(\text{BaCa})\text{CO}_3$ , alstonite  $(\text{BaCa})\text{SO}_4$ , and barytocelestine  $(\text{BaSrCa})\text{SO}_4$ .

<sup>2</sup> By Suter and Redlich of the Elektrochemische-Werke, Bitterfeld.

<sup>3</sup> Muthmann, L. Weiss, and Metzger (*Ann.* (1907), 355, 137) give the value 1.415.

## OXIDES AND SULPHIDES

(The oxides of the type  $M''O$  all result from the direct union of their elements, but are usually prepared by decomposing the hydroxides, carbonates, or nitrates by heat.) The ease with which these compounds are thus decomposed decreases in passing from calcium to barium. For instance, the hydroxides of strontium and barium only part with water on being heated strongly in a current of air; calcium hydroxide, however, commences to lose water at  $100^\circ$ . Again, calcium carbonate is decomposed into the oxide and carbon dioxide at a low red heat, whereas a white heat is required to decompose barium carbonate. [Barium oxide is best obtained by ignition of the nitrate, or by reduction of the carbonate with carbon.]

As regards the effect of heat on the nitrates of groups I A and II A, it is interesting to note that it is only the alkali nitrates which yield nitrites on ignition,<sup>1</sup> the less positive elements of II A forming the oxides. In general, a nitrate other than those of group I A yields, on heating, the oxide of the metal or the metal itself.

(The oxides of calcium, strontium, and barium are refractory solids; barium oxide fuses in the oxyhydrogen flame and calcium oxide can be fused in the electric furnace; it may also be fused, and even vaporized, at the temperature of aluminium burning in oxygen, which reaches  $10,000^\circ$ .)

These oxides all readily unite with water (slake), giving the hydroxides  $M(OH)_2$ . Lime on slaking may reach a temperature of  $150^\circ$ , but baryta may actually become incandescent.) The greater affinity of barium oxide for water, and the greater stability of the hydroxide as compared with the calcium compound, illustrates the increase in the basigenic properties of these metals with increase in atomic weight. The solubility of the hydroxides similarly increases; 100 parts of water at  $15^\circ$  dissolve

$Ca(OH)_2$   
0.127

$Sr(OH)_2$   
0.57

$Ba(OH)_2$   
2.89.

<sup>1</sup> Silver nitrate first yields nitrite, which easily passes into metal.

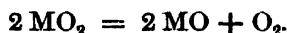
Calcium hydroxide is rather less soluble in hot than in cold water; the solubility of strontium hydroxide, and especially of barium hydroxide, increases rapidly with rise of temperature.

Each of these hydroxides can be obtained crystalline from its solution;  $\text{Sr}(\text{OH})_2$  and  $\text{Ba}(\text{OH})_2$  separate in isomorphous forms containing  $8 \text{H}_2\text{O}$ .

Solutions of these hydroxides are powerful alkalis, having caustic properties, and readily absorbing carbon dioxide.

**The peroxides  $\text{M}''\text{O}_2$ .**—When solutions of the hydroxides of calcium, strontium, and barium are mixed with a solution of hydrogen peroxide, crystals of the hydrated peroxides  $\text{MO}_2 \cdot 8 \text{H}_2\text{O}$  are deposited. Anhydrous barium peroxide is likewise formed on heating the monoxide in oxygen or in the air (in Brin's process in air at  $700^\circ$  under two atmospheres pressure), but calcium and strontium oxides do not so readily combine with oxygen.

All these peroxides lose oxygen on ignition:



When acted upon by dilute acids they yield salts of the metals and a solution of hydrogen peroxide:



Accepting the constitution  $\text{H.O.O.H}$  for hydrogen peroxide, these compounds fall into the class of superoxides, and are formulated:—



**The sulphides** result from the action of hydrogen sulphide on the heated oxides:



or more readily by the reduction of the sulphates by heating with carbon<sup>1</sup> or hydrogen. They are white or yellowish-

<sup>1</sup> Barium sulphide, thus produced from heavy spar ( $\text{BaSO}_4$ ), is the starting-point for the technical preparation of the barium salts.

white substances, which are phosphorescent; that is, they possess the power of glowing in the dark after exposure to light. Calcium sulphide is known as Cantor's phosphorus, and barium sulphide, which emits an orange-coloured light, as Bononian phosphorus. Strontium sulphide emits light which varies in colour according to its manner of preparation. It is probable that these phenomena are due to the presence of traces of other sulphides, such as those of bismuth and manganese. These sulphides are almost insoluble in, but are decomposed more or less readily by, water, with formation of hydroxide and hydrosulphide, thus:—



or possibly hydroxyhydrosulphide  $\text{M(OH)(SH)}$ .

The sulphides, therefore, are not precipitated by the action of hydrogen sulphide on the hydroxide solutions, but hydrosulphides result, thus:—



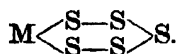
Calcium hydrosulphide may be obtained, crystallized with 6 molecules of water, from the solution formed by the action of hydrogen sulphide on milk of lime. When this compound is heated in a stream of hydrogen sulphide, the sulphide  $\text{CaS}$  results.

The alkaline-earth sulphides resemble the alkali sulphides in the manner in which they are hydrolysed by water, though they differ from them by being practically insoluble in water. As was observed in the case of the alkali sulphides, and many other salts, this hydrolysis is due to the fact that a strong base is combined with a feeble acid.

It was seen in studying the alkali sulphides that they are basic, combining with acidic sulphides, such as those of arsenic and antimony, to form thiosalts. Barium sulphide similarly combines with acidic sulphides, but calcium sulphide does not.

The alkaline-earth or magnesium sulphides form a convenient source of hydrogen sulphide. Calcium sulphide is produced as a by-product in the Leblanc alkali process.

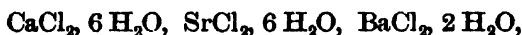
**Polysulphides.**—Just as with the alkali hydrosulphides, the action of excess of sulphur on hot solutions of the alkaline-earth hydrosulphides, as well as of the hydroxides, results in the formation of the polysulphides  $MS_4$  and  $MS_5$ , corresponding with persulphides of hydrogen, and therefore in all probability containing sulphur chains, thus:—



These compounds are decomposed by acids with evolution of  $H_2S$  and precipitation of sulphur.

#### CHLORIDES

The chlorides of calcium, strontium, and barium are of the type  $MCl_2$ , and may be prepared by the methods ordinarily employed for the preparation of salts. They all form crystallohydrates:



and



When these crystallohydrates are strongly heated, in the case of strontium and barium chloride, the anhydrous salts are formed, whilst with calcium chloride partial loss of hydrochloric acid occurs as with magnesium chloride, so that the product is alkaline in reaction, and capable of absorbing carbon dioxide. This fact must be borne in mind in using fused calcium chloride for analytical purposes. The importance of this behaviour of calcium chloride in respect to the systematics of the group has already been indicated.

The solubilities of the chlorides<sup>1</sup> in water diminish from calcium to barium, and calcium chloride alone is deliquescent. Radium chloride, too, is less soluble than barium chloride.

The solubilities of the anhydrous chlorides in absolute alcohol are instructive. Calcium chloride is easily, and strontium chloride sparingly soluble, whilst barium chloride,

<sup>1</sup> It is remarkable that calcium fluoride is insoluble. See Group VII.

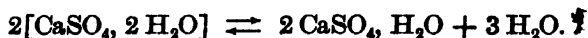


in accordance with its more perfect saline character, is insoluble.

Calcium and strontium chlorides combine with ammonia to form the compounds  $\text{CaCl}_2, 8 \text{NH}_3$ , and  $\text{SrCl}_2, 8 \text{NH}_3$ ; barium chloride appears not to form such a compound.

#### SULPHATES

The sulphates of calcium, strontium, and barium all crystallize in the rhombic system, being isomorphous. (They show progressive insolubility in water from calcium to barium, the solubility of barium sulphate being exceedingly small. Calcium sulphate is more soluble in water at about 40° than at any other temperature, and strontium sulphate is less soluble in hot than in cold water,) being precipitated from a cold solution on boiling. Precipitated barium sulphate is an extremely fine powder, but becomes distinctly crystalline when heated or allowed to stand in contact with water. (Calcium sulphate alone crystallizes with water of crystallization. Gypsum is  $\text{CaSO}_4, 2 \text{H}_2\text{O}$ , and another hydrate,  $2 \text{CaSO}_4, \text{H}_2\text{O}$ , exists. The manufacture and setting of plaster of Paris depend on the reversible reaction



Calcium sulphate is soluble in hot concentrated hydrochloric acid solution, from which it crystallizes again on cooling in silky needles of  $\text{CaSO}_4, 2 \text{H}_2\text{O}$ . The sulphates of strontium and barium are not known to form crystallo-hydrates; strontium sulphate is slightly soluble, and barium sulphate almost insoluble, in concentrated hydrochloric acid.)

Calcium sulphate forms a double salt with potassium sulphate,  $\text{CaSO}_4, \text{K}_2\text{SO}_4, \text{H}_2\text{O}$ , in which a molecule of  $\text{K}_2\text{SO}_4$  takes the place of a molecule of water in the dihydrate; and strontium sulphate also forms a compound with potassium sulphate of somewhat doubtful composition, whilst barium sulphate is not known to combine with alkali sulphates. Calcium sulphate is soluble in concentrated ammonium-sulphate solution, owing to the formation of a double salt,

whereas strontium and barium sulphates are insoluble. This difference is made use of as a process of analytical separation. Each of these sulphates dissolves in concentrated sulphuric acid, acid sulphates of the type  $\text{MH}_2(\text{SO}_4)_2$  being formed, which are decomposed by water.

Most of the facts concerning alkaline-earth sulphates recorded in the preceding paragraphs illustrate the gradation of properties from calcium to barium, in accordance with the increase of electro-positiveness with rise of atomic weight.

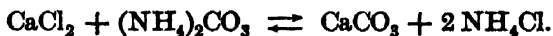
#### OTHER SALTS

Of the other salts the carbonates and phosphates may be briefly noticed.

Calcium carbonate as aragonite, strontium carbonate as strontianite, and barium carbonate as witherite are isomorphous. The pure salts are almost but not quite insoluble in water. Pure precipitated calcium carbonate imparts an alkaline reaction to water, the very small amount dissolved suffering hydrolysis, thus:—



The reactions by which the carbonates are precipitated from the chloride solutions by ammonium carbonate are reversible, thus, *e.g.*:—



The precipitation is therefore rendered more complete by the use of excess of the carbonate solution; and, conversely, excess of ammonium chloride redissolves the precipitate. This reaction accounts for the incomplete precipitation of the alkaline-earth metals by ammonium carbonate, and is perceptible more especially with calcium compounds.

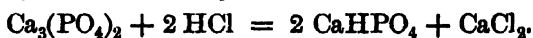
When calcium, strontium, or barium carbonate is suspended in water, and carbon dioxide is passed into the liquid, bicarbonate is formed in solution. These solutions, on evaporation, decompose with loss of carbon dioxide and precipitation of carbonate, though unstable solid bicarbonates of calcium and

barium are said to exist.<sup>1</sup> The solution of calcium carbonate in carbonic acid accounts for the temporary hardness of water. No reliable data are available to indicate the relative stabilities or solubilities of these bicarbonates. That they are less stable than the bicarbonates of the alkalis shows that the power of a metal to form bicarbonate depends upon electro-positiveness. The converse of this is manifested in the formation of basic carbonates, as in the case of magnesium and zinc.

Of the **phosphates**, those of calcium are important. A solution of ordinary sodium phosphate, which is alkaline in reaction, precipitates normal phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , from calcium-chloride solution, thus:—



which, on standing, is gradually converted into monohydrogen calcium phosphate,  $\text{CaHPO}_4$ , thus:—



This salt, which, when formed in the cold, crystallizes with 2 molecules of water, is hydrolysed by water into  $\text{Ca}_3(\text{PO}_4)_2$  and free phosphoric acid.

Normal calcium phosphate itself is hydrolysed on prolonged treatment with water into a more basic insoluble portion, and a more acidic portion, which dissolves, giving an acid solution. In this respect calcium presents a marked contrast to the alkali metals, for normal sodium phosphate is soluble in water, and is hydrolysed, producing an alkaline solution, owing to the powerful basigenic properties of sodium.

Normal calcium phosphate is the main constituent of bone ash. It is soluble in feeble acids, such as acetic, and even to some extent in carbonic acid; it is also soluble, like calcium carbonate, in certain ammonium salts.

Tetra-hydrogen calcium phosphate,  $\text{CaH}_4(\text{PO}_4)_2$ , is produced by the action of sulphuric acid on  $\text{Ca}_3(\text{PO}_4)_2$ . It is soluble in water, and is a constituent of superphosphate of lime.

The **nitrates** and **chlorates** of these metals are soluble salts.

Many salts of calcium, especially organic salts such as the

<sup>1</sup> E. H. Keiser and others, *J. Amer. Chem. Soc.*, 1908, 30, 1711, 1714.

acetate and butyrate, resemble the sulphate in being less soluble in hot than in cold water. They are therefore obtained crystalline by allowing their solutions to evaporate spontaneously at atmospheric temperature.

### ZINC, CADMIUM, AND MERCURY

These metals are related to the metals of the calcium group in the same general manner as are copper, silver, and gold to those of the potassium group. As their positions in series may be taken to indicate, the resemblance between the sub-groups is not so well marked here as it is in the central groups. It is, however, better defined than in Group I, being shown by the preservation of the group valency of two. As already stated, magnesium forms the link between the alkaline-earth metals and the less positive metals of sub-group II B. These metals further differ from their analogues in sub-group A in forming volatile organo-metallic derivatives. With rise in atomic weight the change here, as in Group IB, is from more to less electro-positive. Judged, however, by the properties of their hydroxides, zinc is less basigenic than cadmium. The resemblance of mercury to cadmium is less close than that of cadmium to zinc, as the gap in the table indicates, and it will therefore be convenient to deal first with the chemical properties of the two former metals.

**Physical Properties.**—The physical properties of the metals of Group II B show regular gradation. The densities increase whilst the melting and boiling points decrease with increase of atomic weight, as shown in the appended table. In the state of vapours, the molecules are all monatomic.

	Zn	Cd	Hg
Atomic weight.....	65·37	112·40	200·0
Density .....	7·19	8·7	13·59
<sup>1</sup> Melting-point .....	412°	320°	—39·4°
Boiling-point.....	920°	778°	360°

<sup>1</sup> The exact values for melting and boiling points of metals cannot as a rule be stated with certainty, since these differ within small limits according to different observers. As a rule the more commonly accepted values are given.

**The Metals Zinc and Cadmium** are associated with one another as sulphides in zinc blende, which is chiefly  $\text{ZnS}$ .

In the reduction by means of carbon of the oxides, formed by roasting the sulphides, the more volatile cadmium passes over first, and is purified by redistillation.

Both metals on ignition in the air burn to the monoxides; they are slowly oxidized in ordinary moist air, but do not so readily decompose water on heating as does magnesium. When immersed in water containing oxygen and carbonic acid, zinc, like lead, is slowly converted into basic carbonate. These metals are readily attacked by acids; ordinary dilute acids, except nitric acid, evolve hydrogen. Zinc is dissolved by alkalis with evolution of hydrogen. The comparison of beryllium, magnesium, and zinc with reference to their behaviour towards nitric acid and alkalis is interesting. With nitric acid there is respectively no action, evolution of gases containing hydrogen, and evolution of gases not containing hydrogen; and with alkali, there is respectively solution with evolution of hydrogen, no action, and solution with evolution of hydrogen. From these latter facts it may be concluded that the rise in basigenic properties from beryllium to magnesium is followed by a fall from magnesium to zinc. It is singular that beryllium (with aluminium) and zinc, which behave similarly with alkalis, differ entirely in their behaviour towards nitric acid.

**The Monoxides  $\text{ZnO}$  and  $\text{CdO}$**  are basic, yielding the salts of the metals on treatment with acids, and correspond with the hydroxides  $\text{Zn(OH)}_2$  and  $\text{Cd(OH)}_2$ . These cannot, however, be prepared by the union of the oxides with water, but are obtained by precipitation of the soluble salts with alkali hydroxides. Zinc hydroxide differs from cadmium hydroxide in being soluble in caustic alkalis, just as zinc is soluble and cadmium insoluble in the same reagents; zincates<sup>1</sup>  $\text{Zn(OM')}_2$  are formed in each case. The conclusion that cadmium is more basigenic than zinc, although in accordance with the general rule regarding simultaneous increase of metallic properties and atomic weight, is not in agreement with the

<sup>1</sup> See, however, note on p. 48.

positions of the elements in the electro-potential series. Both zinc and cadmium hydroxides are soluble in ammonia. This is due, not to acidic properties of the hydroxides, but to the formation of complex "ammines" of the type  $M(NH_3)_n(OH)_2$ .

The Peroxides  $ZnO_2$  and  $CdO_2$  are formed when the hydroxides are moistened with hydrogen-peroxide solution.

They are thus superoxides, having the constitution  $M \begin{array}{c} \diagup O \\ \diagdown O \end{array}$ ,

and are easily decomposed, giving off oxygen. The superoxides of magnesium, zinc, and cadmium are less stable than those of the alkaline-earth metals; thus the formation of stable superoxides is a criterion of the electro-positive or basigenic properties of a metal.

**Cadmous Oxide and its Derivatives.**—It was observed in the case of copper and gold, in Group I A, that two series of salts are known, namely, the cuprous and cupric and the aurous and auric salts, and also that a sub-chloride of silver probably exists. Moreover mercury, the last member of the sub-group now under consideration, forms two well-defined series of salts. It is of interest, therefore, to enquire whether zinc and cadmium form oxides and derivatives lower than the monoxides. Cadmium is known to form such compounds, but not zinc. When cadmic chloride is heated with cadmium, cadmous chloride is formed; and this, on treatment with water, gives a white precipitate of cadmous hydroxide,  $CdOH$ , which, on gentle ignition, yields cadmous oxide as a yellow powder.

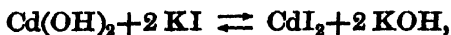
The sulphides of zinc and cadmium are insoluble in water, and differ from the alkaline-earth sulphides in not being hydrolysed. They are precipitated from neutral-salt solutions by hydrogen sulphide, zinc sulphide being white, and cadmium sulphide yellow. Zinc sulphide is soluble in dilute mineral acids, though not in acetic acid; in order, therefore, to secure its complete precipitation by hydrogen sulphide, ammonia or ammonium acetate must be added in excess. Cadmium sulphide, though less soluble than zinc sulphide, is dissolved by a large quantity of dilute hydrochloric or sulphuric acid,

Neither of these sulphides is acidic. The fact that zinc sulphide does not dissolve in alkalis, while zinc oxide does,<sup>1</sup> manifests the feebleness of the electro-negative or non-metallic properties of sulphur as compared with oxygen.

**Halides.**—The halides of zinc and cadmium may be prepared by the direct union of the elements, as well as by the action of solutions of the halogen acids on the metals or their oxides or carbonates. These salts are all solids which melt at moderately low temperatures, and may sometimes be boiled without decomposition, when they sublime in distinct crystals. They are all very soluble in water except the fluorides (*cf.*  $\text{CaF}_2$ ), and likewise dissolve more or less readily in alcohol and ether. Zinc chloride is a white deliquescent mass, which is a powerful dehydrating agent. It may crystallize with one molecule of water. When its solution is evaporated hydrochloric acid is lost, and mixtures of basic chloride  $\text{Zn}(\text{OH})\text{Cl}$  and hydroxide are formed (*cf.*  $\text{MgCl}_2$ ). Zinc iodide, when exposed to the air, deliquesces and absorbs oxygen, losing iodine. The halides of cadmium, in accordance with the more basigenic character of the metal, do not undergo this kind of change.

These halides, as might be anticipated from their other properties, form numerous double salts with alkali halides. They also combine with ammonia, forming, *e.g.*,  $\text{ZnCl}_2 \cdot 2\text{NH}_3$ <sup>2</sup> and  $\text{CdCl}_2 \cdot 2\text{NH}_3$ , and likewise, with hydroxylamine, forming the compounds  $\text{ZnCl}_2 \cdot 2\text{NH}_2\text{OH}$  and  $\text{CdCl}_2 \cdot 2\text{NH}_2\text{OH}$ .

A characteristic of the halides of cadmium, which is further shown in the halides and other compounds of mercury, is the small degree of their electrolytic dissociation in aqueous solution. The stability of these halides towards water is probably partly due to this cause. The above property may be illustrated, according to Ostwald, in the case of cadmium iodide by adding potassium-iodide solution to water in which cadmium hydroxide is suspended. The following reaction takes place:—



<sup>1</sup> See, however, note on p. 48.

<sup>2</sup> For a discussion of these and allied compounds, see end of Chapter XII.

but, owing to the non-dissociation of cadmium iodide, the potassium hydroxide produced cannot readily act upon it, and the solution becomes alkaline.

**Carbonates.**—When alkali carbonates act on solutions of zinc or cadmium salts, basic carbonates of varying composition are formed. Normal zinc carbonate is known as the mineral calamine, and also is precipitated from solutions of zinc salts by potassium hydrogen carbonate, that is, when excess of carbonic acid is employed so as to prevent hydrolysis. Thus zinc carbonate resembles magnesium carbonate in properties, though in accordance with the less basigenic character of zinc the normal carbonate is not obtained from solution like hydrated magnesium carbonate. Cadmium is not known to form a normal carbonate.

Of the **sulphates**, that of zinc,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , is isomorphous with magnesium sulphate. Its solution in water differs from that of magnesium sulphate in possessing an acid reaction due to incipient hydrolysis. A basic salt is produced by ignition, with loss of sulphur dioxide and oxygen. Cadmium sulphate departs from the form presented by magnesium and zinc sulphates, its crystals consisting of  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ , or  $\text{CdSO}_4 \cdot \text{H}_2\text{O}$ . Its cold aqueous solution reacts neutral, but becomes faintly acid when boiled. Zinc sulphate forms double salts with the alkali sulphates of the type  $\text{ZnSO}_4 \cdot \text{M}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ; cadmium sulphate, with some difficulty, forms similar, isomorphous, double salts.

Zinc sulphate forms ammoniacal compounds, such as  $\text{ZnSO}_4 \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O}$ , whilst the anhydrous salt absorbs ammonia, yielding  $\text{ZnSO}_4 \cdot 5\text{NH}_3$ . Cadmium sulphate likewise forms compounds with ammonia.

## MERCURY

Mercury, like gold and thallium, forms two series of compounds: the **mercurous** corresponding with the oxide  $\text{Hg}_2\text{O}$ , and the **mercuric** corresponding with  $\text{HgO}$ . It differs in this respect from the other members of group II, excepting cadmium, which forms the cadmous salts; but this characteristic



finds many parallels in other groups. In most other cases of elements forming more than one series of compounds, the different series owe their existence to a variation in the active valency of the element. In the case of mercury, however, this is probably not the case. Mercurous chloride, when vaporized under ordinary circumstances, is completely dissociated into mercuric chloride and mercury; but when dried most carefully gives, according to Baker,<sup>1</sup> a vapour of the molecular composition  $\text{Hg}_2\text{Cl}_2$ , in which the metal is divalent. It is probable, therefore, that the difference between mercurous and mercuric compounds is to be referred to a difference in the mass rather than the valency of the metallic radicle in the two cases. As will be seen later, mercurous are analogous to cuprous compounds.

Besides forming two well-defined series of compounds, mercury differs from zinc and cadmium in the ease with which its oxides are decomposed by heat, and recalls in this respect its predecessors in series, osmium, iridium, platinum, and gold. Thus mercury occurs native, and its chief natural compound, cinnabar, or mercuric sulphide, easily yields the metal on simply heating in the air,



Mercury is undoubtedly less electro-positive than cadmium or zinc, as is shown by the relative position of the elements in the electro-potential series; it is also less basigenic, as judged by comparison of the general chemical properties of the three elements. Thus mercury does not displace hydrogen from dilute hydrochloric and sulphuric acids, behaving, in this respect, similarly to copper. Indeed mercury is even less electro-positive than copper, as is shown by its displacement from salt solutions by the latter metal.

#### MERCUROUS COMPOUNDS

The oxide  $\text{Hg}_2\text{O}$  is formed as a black powder when alkali-hydroxide solutions are added to mercurous salts. No corre-

<sup>1</sup> *Chem. Soc. Trans.*, lxxvii (1900), 646.

sponding hydroxide is known, and in this respect mercury differs from copper. Moreover, instead of being oxidized completely to mercuric oxide on exposure to air, mercurous oxide splits up into mercuric oxide and metallic mercury. Mercurous sulphide is even more unstable, and has never been isolated, a mixture of mercuric sulphide and mercury resulting from the action of hydrogen sulphide on mercurous salts. Mercurous oxide is a feebly basic oxide which nevertheless displays no acidic properties.

Of the **halides**, **mercurous chloride**,  $\text{Hg}_2\text{Cl}_2$  or calomel, which is volatile, is prepared by heating together mercuric chloride and mercury, or a mixture of mercuric sulphate and mercury with sodium chloride. It may be obtained in quadratic plates, and is fairly stable towards water, probably on account of its extremely small solubility. When, however, it is boiled for a long time with water, or with concentrated hydrochloric acid, some passes into solution as mercuric chloride, while mercury is precipitated. This illustrates a tendency towards the same manner of decomposition that characterizes the oxide, and which is further illustrated by the dissociation which this compound undergoes when heated.

**Mercurous bromide**,  $\text{Hg}_2\text{Br}_2$ , and **iodide**,  $\text{Hg}_2\text{I}_2$ , are similar in properties to the chloride. Both may be obtained crystalline; the bromide is white and the iodide yellow.

The greenish precipitate generally obtained on adding potassium iodide solution to a mercurous salt contains finely divided mercury.<sup>1</sup> Mercurous fluoride, in contrast to the other halides, is soluble in water, and readily undergoes hydrolysis.

**Mercurous sulphate**,  $\text{Hg}_2\text{SO}_4$ , formed as a white crystalline powder by the action of concentrated sulphuric acid on excess of mercury, is almost insoluble in water, and is precipitated by adding sulphuric acid to a solution of mercurous nitrate. It is fairly stable towards heat, melting unchanged, but is hydrolysed by water, with production of basic sulphate.

<sup>1</sup> This is formed by the decomposition of  $\text{Hg}_2\text{I}_2$  in presence of excess of KI, thus:  
 $\text{Hg}_2\text{I}_2 + 2\text{KI} = \text{K}_2\text{HgI}_4 + \text{Hg}$   
 If the KI solution is dilute, the precipitate is yellow, and consists only of  $\text{Hg}_2\text{I}_2$ ; if KI is added in excess, only mercury remains in the precipitate.

**Mercurous nitrate**,  $\text{Hg}_2(\text{NO}_3)_2$ , is formed when cold, dilute nitric acid acts on mercury. Water partially hydrolyses it.

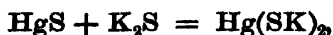
**Mercurous carbonate**,  $\text{Hg}_2\text{CO}_3$ , is precipitated as a yellow powder when potassium hydrogen carbonate is added to a solution of a mercurous salt. As might be anticipated, it easily loses carbon dioxide when gently heated, and leaves a mixture of mercuric oxide and mercury. If a solution of a normal carbonate is used for the precipitation, decomposition takes place at atmospheric temperature, so unstable is mercurous carbonate. A comparison of the carbonates of zinc and cadmium further illustrates the inferior electro-positiveness of mercury.

#### MERCURIC COMPOUNDS

**Mercuric oxide**,  $\text{HgO}$ , is precipitated from solution of a mercuric salt, by excess of alkali hydroxide, as a yellow powder. Probably the hydroxide is first formed, but is exceedingly unstable. The oxide varies in colour from yellow to red; when precipitated from hot solution it is orange, and when obtained by the ignition of the nitrate or of the metal in air, it is red and distinctly crystalline. The difference in colour probably depends on the state of sub-division, that which is most finely divided being most active chemically; the yellow variety is employed in preference to the red, for instance, in the preparation of chlorine monoxide and hypochlorous acid. The yellow form passes into the red at  $400^\circ$ . It is slightly soluble in water, giving an alkaline reaction and possessing no acidic properties. It is decomposed into mercury and oxygen when strongly heated, first turning black. It thus closely resembles silver oxide in chemical properties.

**Mercuric sulphide**,  $\text{HgS}$ , which occurs naturally as cinnabar, is formed eventually as a black<sup>c</sup> amorphous precipitate, when hydrogen sulphide gas is passed through a solution of a mercuric salt, unstable combinations of sulphide and other salt being first produced. Whilst mercuric oxide appears to possess no acidic properties, the sulphide is very feebly acidic.

This is manifested by its solubility in concentrated alkali sulphide and polysulphide solutions, whilst it is insoluble in the corresponding hydroxides. Unstable thiosalts are produced when mercuric sulphide is dissolved, thus:—



but these are decomposed by dilution and boiling. A red crystalline variety of mercuric sulphide, known as vermilion, is more stable and less soluble than the black form. On this account, and because of the solubility of the sulphide in potassium sulphide, contact with a solution of the latter gradually converts the black into the red variety. When either form is heated a black sublimate is obtained, according to the rule that the less stable form is first produced. This, however, is converted into the red form by the mechanical agitation of scratching. As might be expected, cinnabar, the natural form of mercuric sulphide, consists of the more stable red kind.

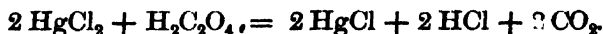
**Mercuric chloride**,  $\text{HgCl}_2$ , prepared by sublimation of a mixture of mercuric sulphate and sodium chloride, crystallizes in needles, is soluble in water and very poisonous, and is known as corrosive sublimate. The aqueous solution of this salt possesses but a faintly acid reaction and shows no signs of hydrolysis. It thus differs from the mercuric oxyalts, which are freely hydrolysed by water. The chloride does not, however, behave like the alkali and alkaline-earth chlorides, since it is soluble in alcohol and ether. Moreover, by a determination of its electric conductivity, it is proved to be but slightly ionised, and this is the cause of its stability towards water. It is also stable towards strong sulphuric acid, like non-metallic chlorides, and is more soluble in strong hydrochloric acid than in water, owing to the formation of the compound  $\text{HHgCl}_3$ . It also readily forms double salts with alkali chlorides such as  $\text{KCl}$ ,  $\text{HgCl}_2$ ,  $\text{H}_2\text{O}$ , and  $2\text{KCl}$ ,  $\text{HgCl}_2$ ,  $\text{H}_2\text{O}$ . When mercuric oxide is shaken with potassium-chloride solution, the liquid becomes alkaline on account of the following reaction:—



the cause of which is the slight ionisation of mercuric chloride. Conversely the precipitation of mercuric oxide from the chloride solution by alkali hydroxide is never quite complete.

Various basic chlorides are formed by the union of the chloride and oxide.

Mercuric chloride is easily reduced to mercurous chloride in aqueous solution, for instance, by oxalic acid:



When stronger reducing agents, such as stannous chloride, are employed, metallic mercury is eventually produced.

The properties of mercuric bromide call for little remark. It is white, and sparingly soluble in water, being ionised to a less extent than the chloride, and more easily forming complex salts.

**Mercuric iodide** exists in two forms, being *enantiotropic*, like the sulphide. The red form is the more stable at ordinary temperature, but above 126° the stability of the yellow form is greater. It is very slightly soluble in water, being precipitated when potassium iodide is added to a solution of a mercuric salt. Whether produced by precipitation or sublimation the less stable yellow form first appears, but gradually changes into the more stable red form. This salt is readily soluble in alcohol. It also combines with potassium iodide, forming the compound  $\text{K}_2\text{HgI}_4$ , consisting of lemon-yellow crystals. This compound contains the stable ion  $\text{HgI}_4$ , and exists in Nessler's solution together with potassium hydroxide, not being decomposed by this substance.

**Mercuric cyanide**,  $\text{Hg}(\text{CN})_2$ , was obtained by Scheele by boiling water with Prussian blue and mercuric oxide, ferric oxide being precipitated and mercuric cyanide passing into solution. This reaction is analogous to that by which mercuric chloride is produced from mercuric oxide and potassium chloride, being due to the slight ionisation of the mercuric salt, which, as soon as formed, ceases to participate in the reaction. The cyanide solution is indeed practically a non-electrolyte, and is not precipitated by alkali carbonate or

hydroxide solution, nor is the solid cyanide decomposed by dilute sulphuric acid; hydrogen sulphide, and the halogen acids, however, decompose the salt. The fact that mercuric cyanide is even less ionised than the halides is connected with the feebly acid nature of hydrocyanic acid itself. This salt yields mercury and cyanogen gas when heated, and forms various basic and double salts.

**Mercuric sulphate and nitrate**, obtained by the action of the concentrated acids on mercury, are rapidly hydrolysed by water. The sulphate produces the yellow "Turpeth mineral"  $\text{Hg}_8\text{SO}_6$ ,



which is sometimes considered to be the ortho-sulphate, that is, a derivative of  $\text{S}(\text{OH})_6$ . The nitrate in contact with water gives rise to the basic salt  $\text{Hg}(\text{NO}_3)\text{OH}$ , and finally the oxide. Only basic carbonates are known, but these are not completely hydrolysed by water.

#### AMMONIACAL MERCURIC COMPOUNDS

When ammonia is added to a solution of mercuric chloride, a white precipitate is obtained which is not mercuric hydroxide but contains nitrogen and chlorine; with mercurous chloride a black powder results, but this may be shown to be a mixture of a nitrogenous mercuric compound and metallic mercury; such nitrogenous mercurous compounds probably do not exist.

According to Rammelsberg<sup>1</sup> and Pesci,<sup>2</sup> the above compound contains the monovalent radicle  $(\text{NHg}'_2)$  in which two atoms of mercury have taken the place of four atoms of hydrogen in ammonium.

A series of such compounds is known. The hydrated hydroxide,  $\text{NHg}_2\text{OH}$ ,  $\text{H}_2\text{O}$ , is obtained as a pale-yellow powder, known as Millon's base, by the action of dilute ammonia on yellow mercuric oxide. This substance on warming loses water, forming first the hydroxide  $\text{NHg}_2\text{OH}$ , and then the

<sup>1</sup> *J. Pr. Chem.* xxxviii, 508.

<sup>2</sup> *Z. Anorg. Chem.* xxi, 361.

oxide  $(\text{NHg}_2)_2\text{O}$ , whilst alcoholic hydrochloric acid produces the chloride  $\text{NHg}_2\text{Cl}$ . The hydrated iodide  $\text{NHg}_2\text{I}$ ,  $\text{H}_2\text{O}$  is the brown substance formed in Nessler's test for ammonia.

According to this view of the constitution of these compounds, "infusible white precipitate", obtained by precipitating mercuric chloride with ammonia, which has the empirical composition  $\text{NHgH}_2\text{Cl}$ , is  $\text{NHg}_2\text{Cl}$ ,  $\text{NH}_4\text{Cl}$ ; whilst "fusible white precipitate" formed by boiling the above with ammonium-chloride solution, and which possesses the empirical composition  $\text{N}_2\text{HgH}_6\text{Cl}_2$ , is  $\text{NHg}_2\text{Cl}$ ,  $3\text{NH}_4\text{Cl}$ .<sup>1</sup> Infusible white precipitate when heated breaks up below a red heat into mercurous chloride, nitrogen, and ammonia; while fusible white precipitate yields mercurous chloride, mercuric chloride, ammonium chloride, nitrogen, and ammonia.

The final stage in the substitution of hydrogen by mercury is realized in mercuric nitride,  $\text{N}_2\text{Hg}_3$ , which results from the action of dry ammonia on mercuric oxide at  $130^\circ$ , as an explosive compound, decomposed by alkalis with evolution of ammonia (*cf.* magnesium nitride).

<sup>1</sup> Another view of the constitution of these compounds has been put forward by Hofmann and Marburg (*Z. Anorg. Chem.* xxlii, 126). According to these chemists infusible precipitate is  $\text{Hg} \begin{smallmatrix} \text{NH}_2 \\ \text{Cl} \end{smallmatrix}$ , fusible precipitate  $\text{Hg} \begin{smallmatrix} \text{NH}_2\text{Cl} \\ \text{NH}_3\text{Cl} \end{smallmatrix}$ , Millon's base  $\text{HO} \cdot \text{Hg} \begin{smallmatrix} \text{NH}_2 \\ \text{OH} \end{smallmatrix}$ , and the simple hydroxide  $\text{O} \begin{smallmatrix} \text{Hg} \\ \text{Hg} \end{smallmatrix} \text{NH}_2 \cdot \text{OH}$ . These formulæ represent three distinct types of compound:

(i) Amidochloride, characteristic rather of acid derivatives; *e.g.*  $\text{CO} \begin{smallmatrix} \text{NH}_2 \\ \text{Cl} \end{smallmatrix}$ .

(ii) Ammines, analogous to those formed by zinc and other metals, *e.g.*



(iii) Substituted ammonium derivatives, as supposed by Rammelsberg and Pesci.

If mercury does indeed form compounds belonging to each of these types, the phenomenon is remarkable.

No significance from the point of view of the periodic law can safely be attached to the existence of these nitrogenous mercuric compounds until their constitution is settled beyond controversy.

## CHAPTER VII

## GROUP III

SUB-GROUP A		SUB-GROUP B
	B (11·0)	
	Al (27·1)	
Sc (44·1)		Ga (69·9)
Y (89·0)		In (114·8)
La (139·0)		
		Tl (204·0)

Boron and aluminium, the typical elements of this group, are more nearly related to the elements of sub-group B than to those of sub-group A. These two elements, together with gallium, indium, and thallium, will therefore be considered as constituting sub-group B, whilst in the more positive sub-group A are included the elements scandium, yttrium, and lanthanum, which, together with cerium and thorium in Group IV, are among the better known and better characterized of the class known as the rare earths. The following elements<sup>1</sup> of the rare earths lie between cerium (140·25) and tantalum (181·0):—

Praseodymium (Pr).....	140·6
Neodymium (Nd).....	144·3
Samarium (Sm).....	150·4
Europium (Eu).....	152·0
Gadolinium (Gd).....	157·3
Terbium (Tb).....	159·2
Dysprosium (Dy).....	162·5
Erbium (Er).....	167·4
Thulium (Tm).....	168·5
Neo-Ytterbium (Yb).....	172·0
Lutecium (Lu).....	174·0

These substances are encountered in exceedingly rare minerals in the form of silicates such as gadolinite (YCePrNdLa), cerite (CePrNdLa), or niobates, tantalates, phosphates, fluorides, and uranates, such as samarskite, which contains Ta<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5</sub>, UO<sub>3</sub> and Ce, Pr, Nd, La, and Y.

Owing to the scarcity of the minerals containing these rare

<sup>1</sup> Only these are at present (1911) recognized as elements.



earths, and the close similarity between the oxides and salts of the elements they contain, the difficulty of effecting such complete separation as would lead to definite characterization of these elements is very great.

The processes available are those of fractionation; for instance, advantage is taken of the variation in decomposition temperature of the nitrates, or fractional precipitation of the hydroxides by means of ammonia is resorted to, when the less soluble earths will first be deposited; fractional crystallization of salts such as formates and oxalates is also an effective means of separation. The course of the separation may be followed by estimations of the equivalents of the oxides, or by the study of their spark spectra, the latter method indicating that in all probability most of the earths are complex mixtures.<sup>1</sup>

Cerium, lanthanum, praseodymium, neodymium, and samarium have been obtained,<sup>2</sup> by the electrolysis of their fused chlorides, in a condition sufficiently pure for the determination of their densities and melting-points, which are as follows:—

	Dens.		M.P.
Ce .....	7.04	.....	623°
La .....	6.15	.....	810°
Pr.....	6.47	.....	940°
Nd .....	6.96	.....	840°
Sm .....	7.75	.....	—

With regard to the positions of these elements in the periodic system, whilst yttrium and lanthanum possess atomic weights and properties which secure for them appropriate positions in the table, the elements<sup>3</sup> in the above list, whose supposed atomic weights lie close together, must all be interpolated, as previously pointed out, between cerium in Group IV and tantalum in Group V, an arrangement which finds some analogy in the triads of elements constituting the eighth group.

<sup>1</sup> See Chapter IX.

<sup>2</sup> Muthmann and Weiss, *Annalen*, 1904, 331, 1.

<sup>3</sup> The atomic volumes of the five elements, whose densities have been determined, cause the elements to be placed on a descending curve between barium and tantalum.

## SUB-GROUP III B

*Boron, Aluminium, Gallium, Indium, and Thallium*

The positions of boron and aluminium in the group are, on the whole, similar to those of beryllium and magnesium in Group II. Boron is the first element in the second series in which non-metallic characteristics predominate. It is the first element to form a hydride, its oxide scarcely possesses basic properties, behaving entirely as an acidic oxide in its more stable compounds, and the properties of the element itself are those of a non-metal. Aluminium, succeeding magnesium and preceding silicon in series, presents the physical characters of a metal, and is strongly electro-positive, but oxygenic properties are indicated by its feebly acidic hydroxide, and by its chloride. From aluminium to gallium the change is of the same kind as from magnesium to zinc; thus gallium must be regarded as more oxygenic than aluminium,—just as zinc is more so than magnesium,—because its hydroxide is soluble in ammonia as well as in the alkali hydroxides, aluminium hydroxide being almost insoluble in ammonia, and also because gallium alum is more easily hydrolysed by water than aluminium alum. The heavier metals indium and thallium are more basigenic than their predecessors, as will be seen from a comparison of the properties of their oxides and halides. The tendency to form compounds of more than one type, which in the second group was observed to commence with cadmium, and to become well developed with mercury, commences in the third group with gallium, which forms a dichloride, and becomes more pronounced with indium and thallium, indium forming the chlorides  $\text{InCl}$ ,  $\text{InCl}_2$ , and  $\text{InCl}_3$ , and thallium  $\text{TlCl}$  and  $\text{TlCl}_3$ .

The characteristics of these salts and of others related to them will be studied in the systematics of the sub-group.

## PHYSICAL PROPERTIES

The Group III B elements all occur at or immediately following minima in Lothar Meyer's curve of atomic volumes,

the metals being malleable and readily fusible. The physical properties given in the table show the variation within the group.

	B	Al	Ga	In	Tl
Atomic weight....	11.0	27.1	69.9	114.8	204.0
Density .....	2.45	2.68	5.9	7.4	11.8
	amorphous cryst.				
Melting-point.....	very high	660°	30.1°	155°	290°

It will be seen from the table that whilst the densities of these elements gradually rise from aluminium to thallium, in the case of the melting-points there is a sudden fall from aluminium to gallium, followed by a gradual rise again to thallium. The contrast between the melting-points of aluminium and gallium clearly marks the transition from the typical elements to those of the B sub-group, a transition which is scarcely perceptible in the study of chemical properties. The rise in melting-point from gallium onwards is the opposite of what obtains in Group II B, which is exceptional; in the following sub-groups there is also rise of melting-point with rise of atomic weight. The melting-point of gallium is surprisingly low, though an element occupying its position should have a low melting-point.

### BORON

The element boron is obtained either from its trioxide, by reduction with potassium or magnesium, or else by passing the vapour of the trichloride over heated sodium. Thus produced, it is a brown, amorphous powder. It may be obtained in the crystalline or adamantine form, though probably containing some aluminium as an impurity, by crystallization from solution in molten aluminium.

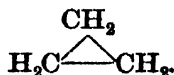
Amorphous boron easily burns in air, forming the trioxide, is oxidized by oxyacids and steam, is dissolved by alkali hydroxides like aluminium, and combines with nitrogen gas when heated in it, forming the nitrate BN. This compound is decomposed by steam thus:— $\text{BN} + 3\text{H}_2\text{O} = \text{B}(\text{OH})_3 + \text{NH}_3$ . The natural occurrence of boric acid and ammonia together in the *suffioni* of Tuscany is probably due to this reaction.

## HYDRIDES

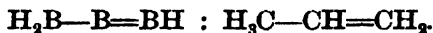
Of the elements of Series 2 boron, in accordance with its negative character, is the first to form a hydride. When magnesium and boron trioxide are heated together in appropriate proportions, the product is chiefly magnesium boride,  $Mg_3B_2$ . When dilute acid is added to this substance a mixture of hydrogen and boron hydride is obtained. By cooling this mixture of gases with liquid air, Ramsay and Hatfield<sup>1</sup> obtained a white crystalline solid which, when gasified, possessed a density of 19.36, and burned with a green flame. This gas consists chiefly of  $B_3H_3$ , which probably possesses a cyclic constitution thus:—



being analogous therefore to trimethylene:



It is known as cyclotriborene. Another triborene probably exists which is unsaturated, and is analogous to propylene:



These hydroborons are analogous to hydrocarbons also in physical and chemical properties, cyclotriborene being a neutral gas practically insoluble in water.  $BH_3$  also probably exists, and possibly a solid hydride  $B_3H$ , which Ramsay and Hatfield think to be the hydrogen analogue of the alkaline-earth borides.

Boron combines with carbon and with silicon at the temperature of the electric furnace, forming the carbide  $B_6C$ , and the silicides  $B_3Si$  and  $B_6Si$ . These compounds are crystalline and very hard, and are unaffected by most chemical reagents. As regards properties, therefore, they belong to the same category as diamond and crystalline boron and silicon.

<sup>1</sup> *Chem. Soc. Proc.* xvii, 152.

Metallic borides likewise may be produced at very high temperatures. They are generally hard substances possessing little chemical activity.

Calcium boride, obtained by the use of the electric furnace, is a hard, black, crystalline powder, which is not acted on by water or dilute hydrochloric acid at ordinary temperature. When fused in the electric furnace it reacts with water with evolution of hydrogen and hydrogen boride. Thus it differs markedly from calcium carbide prepared in an analogous manner.

It appears, therefore, that the hydrides of boron are neutral, inert substances, analogous to many of the hydrides of carbon; so that chemical activity of hydrides only becomes prominent when the fifth group is reached.

Boron alkyls are of the type  $BR_3$ , corresponding to  $BH_3$ . They are not basic, but are oxidized by air and water into alkyl boric acids or their esters.

#### HALIDES

Compounds of boron with all four halogen elements are known; their physical properties are as follows:—

$BF_3$ , a colourless gas condensable to a mobile, colourless liquid.

$BCl_3$ , a colourless liquid, B.P.  $18.2^\circ$ .

$BBr_3$ , a thick, colourless liquid, B.P.  $90.5^\circ$ .

$BI_3$ , white, leafy crystals, M.P.  $43^\circ$ , B.P.  $210^\circ$ .

They are prepared either by the direct union of their elements, or by heating a mixture of the trioxide and charcoal with the halogen



These two methods are those which are general for the preparation of non-metallic halides. In addition, the action of the dry halogen acid upon boron or its trioxide serves for the preparation of the fluoride and chloride, the former being generally obtained by treatment of the trioxide with calcium fluoride and strong sulphuric acid:

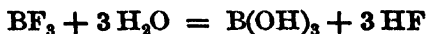


This method is similar to that employed for the preparation of silicon tetrafluoride—not, however, the tetrachloride—but is really more characteristic of the manner of formation of metallic halides, since it is analogous to salt formation.<sup>1</sup>

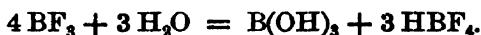
Its realization here is probably due to the volatility of the fluoride and chloride, as well as to the comparative stability of these compounds towards water which is formed in the reaction, this stability being due to the feebly non-metallic character of boron.<sup>1</sup>

In chemical respects these halides nevertheless behave as halanhydrides, that is, they yield the oxyacid and halogen acid when acted on by water, and are not attacked by strong sulphuric acid.

In the case of the fluoride, the hydrofluoric acid produced by its hydrolysis according to the reaction



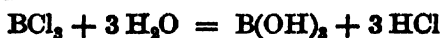
unites with the unchanged substance to produce hydrofluoboric acid,  $\text{HBF}_4$ , so that the complete reaction may be written



A series of salts, the fluoborates, is known, corresponding to this acid; they are decomposed by heat, evolving the trifluoride.<sup>2</sup>

<sup>1</sup>Silicon tetrafluoride behaves in an analogous way with water. Thus is furnished a resemblance in chemical properties between boron and silicon; the resemblance in physical properties is also very close. The union of the fluorides of these elements with hydrofluoric acid in preference to their decomposition by water is due again to the feebly non-metallic character of the elements, and the resulting stability towards water of their fluorides.<sup>1</sup> Boron trifluoride combines with ammonia, forming the compounds  $\text{BF}_3 \cdot \text{NH}_3$ ,  $\text{BF}_3 \cdot 2 \text{NH}_3$ ,  $\text{BF}_3 \cdot 3 \text{NH}_3$ .

The first action of water on boron trichloride results in the formation of a solid crystallohydrate, the decomposition indicated by the equation



requiring the action of excess of water.

The chloride is thus less readily acted on by water than such distinctly non-metallic chlorides as  $\text{PCl}_3$ . In the circumstance of forming a crystallohydrate, boron trichloride resembles stannic chloride, and thus shows the element boron to possess some of the characters of a metalloid. Boron chloride likewise resembles aluminium chloride in its behaviour towards water, though the latter is more saline in its physical properties, as becomes the more metallic character of aluminium.'

#### OXIDE

Boron forms only the typical oxide,  $\text{B}_2\text{O}_3$ , no suboxide or peroxide being known; perborates of the type  $\text{M}'\text{BO}_3$  appear, however, to exist.

**Boron Trioxide**,  $\text{B}_2\text{O}_3$ , is the anhydride of boric acid, from which it may be obtained by heating to redness. It is hygroscopic, passing again into boric acid by absorption of water. It resembles silica in non-volatility, in consequence of which it is able to expel the anhydrides of strong acids such as nitric and sulphuric from their salts on heating; and, as a weak acidic oxide, it forms complex salts with metallic oxides, in which the proportion of acidic oxide may be large, resembling in this respect silica and the acidic oxides of tungsten, molybdenum, and vanadium. It differs, however, from silica in its easy fusibility and power of combining with water; its salts, too, are more fusible than the analogous silicates, being formed in borax beads. Boron trioxide also enters into the composition of some silicates (*e.g.* tourmaline), probably playing the same rôle as its analogue aluminium trioxide, and combines with tungstic anhydride and certain metallic oxides to form complex borotungstates.

Being a feebly acidic oxide, boron trioxide also displays very feebly basic functions. For example, boric acid combines with sulphur trioxide, forming the compound  $\text{B}(\text{HSO}_4)_3$ , and with phosphoric and acetic acids, forming  $\text{BPO}_4$  and  $\text{B}(\text{C}_2\text{H}_3\text{O}_2)_3$  respectively. These compounds are unstable, and are easily hydrolysed by water or dilute acids. The so-called phosphate of boron,  $\text{BPO}_4$ , is, however, insoluble in water and dilute

acids, but is dissolved by alkali hydroxides, forming alkali borate and phosphate. All these compounds, perhaps, are better considered as mixed anhydrides.

#### BORIC ACID

On hydration of the trioxide, or when solutions of the borates are acidified, **orthoboric acid**,  $B(OH)_3$ , is formed. This acid crystallizes from water in pearly plates, is volatile in steam, and colours the Bunsen flame green. It is a very weak acid, like carbonic acid, colouring litmus solution wine red.

At  $100^\circ$  orthoboric acid loses water, forming the first anhydro-acid, which is known as **metaboric acid**; and at  $160^\circ$ , by further loss of water, the second anhydro-acid, known as **pyro-** or **tetraboric acid**, is produced. The relationships of these acids to one another are probably as follows:—

Orthoboric acid  $B(OH)_3$ .

Metaboric acid (1st anhydride)  $B(OH) \begin{array}{c} \diagup O \diagdown \\ \diagdown O \diagup \end{array} B(OH)$ .

Pyroboric acid (2nd anhydride)  $B(OH) \begin{array}{c} \diagup O \diagdown \\ \diagdown O \diagup \end{array} B-O-B \begin{array}{c} \diagup O \diagdown \\ \diagdown O \diagup \end{array} B(OH)$ .

(It may be pointed out that the nomenclature which is customary in the case of these acids is not consistent with that employed elsewhere, *e.g.* in the case of the phosphoric acids, in which the pyro- contains a larger proportion of water than the meta-acid.)

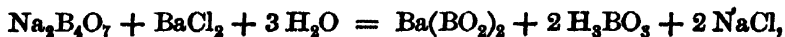
Metaboric acid is often supposed to be  $O=B(OH)$ . In the absence of direct evidence of molecular weight, the formula  $M'BO_2$  will be used for metaborates in what follows.

Few orthoborates are known. The magnesium salt  $Mg_3(BO_3)_2$  exists, and also volatile alkyl orthoborates such as  $B(OC_2H_5)_3$ , which is produced in the familiar test for a borate with alcohol and sulphuric acid. 'Another resemblance between carbonic and boric acids is shown in the fact that the only known ortho-carbonates are alkyl salts.'

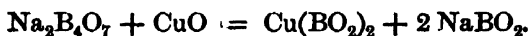
The most stable salts of boric acid are the metaborates. All except those of the alkalis are insoluble in water, and are



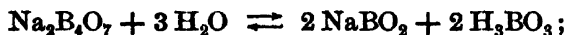
precipitated by adding a solution of borax—although a pyroborate—to a solution of the metallic salt. The following is the reaction by which barium metaborate is precipitated:—



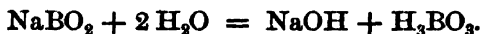
whilst the borax bead reaction, in which fusible cupric metaborate is produced, may be represented thus:—



The best-known salt of pyroboric acid is **borax**,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ . An aqueous solution of this salt is alkaline in reaction on account of hydrolytic dissociation. In concentrated solution the following change probably takes place:—



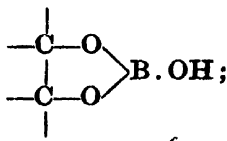
whilst on dilution there is an approximation to complete hydrolysis according to the following reaction:—



Since boric acid, like carbonic acid, does not affect methyl orange, a dilute solution of borax may be titrated with standard mineral acid, by use of this indicator.

Borates still more complex than the above are known. The mineral larderellite,  $(\text{NH}_4)_2\text{B}_8\text{O}_{13}$ , furnishes an example.

Boric acid gives rise to remarkable compounds by combination with organic oxyacids and polyhydric alcohols. In great probability it forms with them ring compounds containing the grouping



and it is likely that the enormous increase in optical activity caused with compounds such as tartaric and malic acids and mannitol is attributable to this ring combination.

**Boron trisulphide**,  $\text{B}_2\text{S}_3$ , is formed by passing the vapour of

carbon disulphide over a heated mixture of boron trioxide and carbon:



It is a white crystalline substance, which like aluminium sulphide is hydrolysed by water. It combines with hydrogen sulphide to form meta-thioboric acid,  $\text{H}_2\text{B}_2\text{S}_4$ , which is also decomposed by water.

### ALUMINIUM, GALLIUM, AND INDIUM

These three metals form a group whose members are closely related, the variation in properties being in accordance with the provisions of the periodic law. It is interesting to recall that by the application of these provisions Mendeléeff was able to indicate the properties of his eka-aluminium, subsequently realized in the element gallium. From the analogy of the second group, gallium would be expected to be somewhat less electro-positive than aluminium, just as zinc is less electro-positive than magnesium, and this is actually the case.

Aluminium is very plentiful in nature, both as oxide and in many common silicates. 'Gallium and indium are widely distributed, but in minute quantities, and chiefly in zinc blends.'

Aluminium oxide is only reducible by electrolysis, or at the temperature of the electric furnace, or else by the use of sodium, 'but the oxides of gallium and indium are easily reduced when heated in a current of hydrogen.' Aluminium is non-volatile even at a high temperature, and its salts do not colour the non-luminous gas flame, though a characteristic spectrum is revealed by the use of the electric arc or spark. 'Gallium compounds colour the non-luminous gas flame slightly, and the spark spectrum contains two violet lines. Indium and its compounds give a characteristic dark-blue colour to the non-luminous gas flame, which shows a well-defined spectrum. It was by means of spectrum analysis that the two latter metals were discovered.'

'None of these metals in the ordinary state is easily acted on by water,' though aluminium in the form of amalgam, when

the protection due to superficial oxidation is prevented, is gradually changed into hydroxide by contact with water, or moist air. 'Dilute hydrochloric and sulphuric acids dissolve all three metals; indium is readily attacked by nitric acid; dilute nitric acid slowly dissolves aluminium, and also gallium, with evolution of nitric oxide; but aluminium is passive towards concentrated nitric acid. Aluminium and gallium, being oxygenic, easily dissolve in alkali-hydroxide solutions, forming aluminates and gallates.' Aluminium, being more oxygenic than zinc, similarly placed in Group II, is able to displace the latter from its solution in alkalis.

### THE HALIDES

Halides of the group type  $M''X_3$  are known in the case of all three metals, and in addition gallium forms a dichloride,  $GaCl_2$ , and indium the chlorides  $InCl_2$  and  $InCl$ . Thus the tendency to form compounds of lower valency than that of the group type, which was observed in Group II B, appears again here. The trihalides are all solid substances, though volatile.

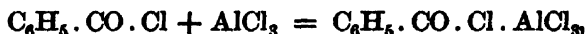
**Aluminium fluoride**,  $AlF_3$ , is less volatile than the other halides of this metal, and is scarcely soluble in water. It furnishes another example of the exceptional properties of fluorides (*cf.*  $AgF$ ,  $CaF_2$ ,  $HgF_2$ ). It dissolves in aqueous hydrofluoric acid, forming hydrofluoaluminic acid,  $H_3AlF_6$ , the sodium salt of which occurs as the mineral cryolite.

The trichlorides all possess properties characteristic of the halides of elements of metalloidal character. Thus they are all volatile, their boiling or subliming points being approximately

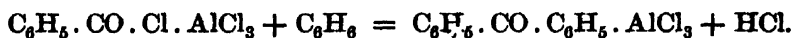
$AlCl_3$	$GaCl_3$	$InCl_3$
183°	220°	446°

**Aluminium chloride** is easily soluble in alcohol and ether. It forms double compounds with ammonia and with metallic halides, for instance,  $NaCl \cdot AlCl_3$ , which is volatile; it also combines with certain acid chlorides, such as phosphorus pentachloride and oxychloride, and also the chlorides of organic acids. This property explains the use of aluminium.

chloride in Friedel and Crafts' method for synthesis of ketones. In this process the acid chloride first unites with aluminium chloride, thus:—



the product then reacting with benzene to form a crystalline compound with evolution of hydrochloric acid:



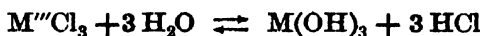
This compound is then decomposed by water and the ketone results.

This explanation does not appear to suffice for the synthesis of benzene homologues from alkyl chlorides and benzene by means of aluminium chloride.

Ferric chloride acts similarly to aluminium chloride, though less efficiently.

All the trichlorides are acted on by water, fuming in moist air. When aluminium chloride separates from solution in excess of hydrochloric acid, it forms  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , which on heating gives the oxide and hydrochloric acid. The solutions of the chlorides in pure water easily lose hydrochloric acid on evaporation, with formation either of basic salts or the oxides.

The reaction



is a reversible one, on account of the intermediate character of the compounds of these metals. A similar reaction is characteristic of arsenious chloride and hydroxide.

This hydrolytic dissociation is further well shown by the behaviour of the soluble basic chlorides of aluminium on dialysis, when a pure suspension<sup>1</sup> of colloidal aluminium hydroxide, the hydrosol of alumina, is formed.

**Aluminium tribromide and tri-iodide**,  $\text{AlBr}_3$  and  $\text{AlI}_3$ , are similar to the trichloride; they are both volatile, and the vapour of  $\text{AlI}_3$  is combustibile. They both form crystallohydrates like the chloride, containing six molecules of water, and are similarly decomposed by heat.

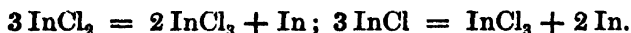
<sup>1</sup> See note, p. 149.

The iodide, like boron tri-iodide, is capable of entering into metathesis with certain chlorine compounds; *e.g.*



#### LOWER CHLORIDES OF GALLIUM AND INDIUM

When gallium trichloride is heated with gallium, and when indium is heated in anhydrous hydrochloric acid, the dichlorides  $\text{GaCl}_2$  and  $\text{InCl}_2$  are formed respectively. Indium dichloride, reacting with metallic indium, yields the volatile monochloride  $\text{InCl}$ . By the action of water both the lower chlorides of indium give the metal and the more stable trichloride:



#### OXIDES AND HYDROXIDES

These are of the group type  $\text{M}'''_2\text{O}_3$  and  $\text{M}'''(\text{OH})_3$ , together with intermediate compounds, no other oxides being known.

The oxides, all of which are formed when the hydroxides and salts of volatile oxyacids are heated, differ from one another in some important respects.

Gallium and indium oxides, in contrast to aluminium oxide, are both easily reduced by carbon and hydrogen, and do not on strong ignition pass into forms insoluble in acids, as does aluminium oxide.

The hydroxides, precipitated by ammonia from their salts, are all colloids, and as such, pass into colloidal suspension<sup>1</sup> in water. Aluminium hydroxide, for example, can exist in a solid form as *hydrogel*, and in colloidal suspension as *hydrosol*, this latter form being obtained by the dialysis of an aqueous solution of aluminium chloride. The hydrosol form of aluminium hydroxide is converted into the hydrogel form by the addition of ammonium chloride; presence of this reagent, therefore, secures the complete precipitation of aluminium hydroxide by ammonia.

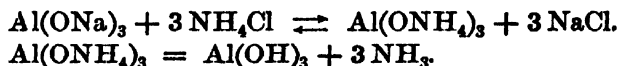
<sup>1</sup> What is commonly called a solution of a colloid is in reality a suspension. Such a "solution" does not possess the physical properties of a dilute solution.

Freshly precipitated alumina is completely hydroxylated, and is easily soluble in dilute acids, but on standing or boiling with water it becomes less soluble, probably owing to formation of  $\text{Al}_2\text{O}(\text{OH})_4$  or  $\text{AlOOH}$ .

The three hydrated forms occur naturally,  $\text{Al}(\text{OH})_3$  as hydrargillite,  $\text{Al}_2\text{O}(\text{OH})_4$  together with iron oxide as bauxite,  $\text{AlOOH}$  as diaspore.

The hydroxides of aluminium, gallium, and indium possess, in addition to their feebly basic, feebly acidic properties. Thus, whilst they all yield solutions of their salts with excess of acid, they are all soluble in alkali hydroxides; gallium hydroxide is also soluble in ammonia, from which it appears to be more acidic than its congeners, a conclusion which is confirmed by the more ready hydrolysis of gallium salts. Of the alkali salts thus produced, the aluminates are best known.

The salts  $\text{NaH}_2\text{AlO}_3$ ,  $\text{Na}_2\text{HAlO}_3$ ,  $\text{Na}_3\text{AlO}_3$ , corresponding to  $\text{H}_3\text{AlO}_3$ , exist. Their aqueous solutions are strongly alkaline on account of hydrolysis, and are decomposed by carbonic acid with precipitation of aluminium hydroxide; ammonium chloride causes a similar precipitation on account of the complete hydrolysis of ammonium aluminate:—



Saline derivatives of  $\text{AlOOH}$  are also well known.  $\text{KAlO}_2$  is produced when aluminium reacts with potassium hydroxide. It is insoluble in alkalis and decomposed by water.  $\text{MgAl}_2\text{O}_4$  occurs as the mineral spinelle.

Solutions of alkali tartrates, citrates, and malates prevent the precipitation of aluminium hydroxide by alkali hydroxide. This phenomenon, which is analogous to that presented in the case of cupric and iron salts, is due to the formation of complex acidic ions containing aluminium, copper, or iron. Just as boric acid forms salts containing an excess of acidic oxide, so also with aluminium the same tendency may be noted. When aluminium oxide and a metallic oxide are strongly ignited with boron trioxide, which serves as a flux,

the latter substance gradually volatilizes, leaving artificial complex aluminates which constitute alumina gems.

Aluminium hydroxide combines with various organic dye-stuffs, forming "lakes".

#### SULPHATES

The sulphates of these three metals of the type  $M'''_2(SO_4)_3$  are formed by the action of excess of sulphuric acid on the oxides or hydroxides; they are all very soluble in water, and suffer hydrolytic dissociation, easily giving rise to basic salts.

**Aluminium sulphate**,  $Al_2(SO_4)_3 \cdot 18H_2O$ , crystallizes in lustrous scales. Its aqueous solution reacts acid, and dissolves magnesium with evolution of hydrogen; it also dissolves aluminium hydroxide, forming basic sulphate, which is eventually deposited.  $Al_2O(SO_4)_2$  has been obtained crystalline.

**Alums**, possessing the general formula  $M'_2SO_4 \cdot R'''_2(SO_4)_3 \cdot 24H_2O$ , are formed by the sulphates of these metals, and are less soluble in water than the single salts. They are isomorphous, crystallizing in regular octahedra; similarly constituted alums are also formed by ferric, chromic, and manganic and other sulphates, and also by analogous selenates. The stability of these double sulphates, as well as their insolubility in water, increases with increase of electro-potential difference between the metals, as was pointed out in Chapter V, page 96. Alums exist as such to a slight extent only in aqueous solution, breaking up more or less into mixtures of the single salts. Various basic alums exist; for instance, the mineral alumstone  $K_2SO_4 \cdot Al_2SO_4(OH)_4$ .

#### OTHER SALTS

Of the other salts, the **nitrates** are soluble in water, that of aluminium being decomposed at  $150^\circ$ , leaving the oxide. **Aluminium phosphate**,  $AlPO_4$ , is easily soluble in dilute hydrochloric, and sparingly soluble in dilute acetic acid. On boiling the latter solution a basic salt is precipitated.

In conformity with their feebly basigenic character, none of these metals yields a carbonate; alkali carbonates precipi-

tate the hydroxides. Similarly, the sulphides are not formed in the wet way, hydroxides resulting when alkali sulphides act on the salt solutions. Indium sulphide,  $\text{In}_2\text{S}_3$ , however, in accordance with the more metallic character of indium, is formed as a yellow precipitate when hydrogen sulphide is passed through a neutral salt solution; but ammonium sulphide converts the precipitate into the white hydrosulphide.

### THALLIUM

Thallium, the element of highest atomic weight of the group, occurs associated with varieties of pyrites in zinc ores, with potassium in carnallite and sylvine, and with silver and copper in the mineral Crookesite. Like gallium and indium it owes its discovery to spectrum analysis, and like them it is easily reducible from its oxides or salts, being usually precipitated from a solution of its sulphate by zinc.

In physical properties thallium closely resembles its successor in series, lead. It has a bluish, lead-like tint, is soft and malleable but not tenacious, and marks paper. It has a density of 11·8, melts at  $290^\circ$ , and is volatile in a stream of hydrogen; lead with a density of 11·34 melts at  $326^\circ$  and is also somewhat volatile. Thallium colours the non-luminous gas flame bright green, its spectrum consisting of a single green line. In this respect it resembles the alkali metals.

The mode of natural occurrence of thallium, together with such varied elements as zinc, potassium, and silver or copper, as well as its physical properties and the position assigned to it in the periodic classification, make the discussion of the chemical properties and analogies of this element a matter of more than usual interest.

Gold and mercury, occupying positions in Groups I and II analogous to that occupied by thallium in Group III, present two series of compounds: the aurous and auric, and the mercurous and mercuric compounds respectively. Thallium likewise forms thallous and thallic compounds of the same types as the aurous and auric derivatives. Now whilst gold, and to some extent mercury, show the feeble reactivity which



is specially characteristic of the eighth group, so that their compounds, especially those of lower valency, are somewhat unstable, the thalious compounds exhibit no such property. These compounds, therefore, are not very similar to the aurous compounds, but resemble instead the compounds of the alkali metals in Group I A, to which they are also related by type. This resemblance, however, although important, does not exhaust the analogies of thalious compounds.

The neighbours of thallium in Groups II and IV are mercury and lead respectively, and it has already been seen that metallic thallium resembles lead. Thalious salts also resemble mercurous and silver, and especially lead salts. Thallic salts, although typical of the third group, of which thallium is a member, are rather unstable; they somewhat resemble auric compounds.

All these relationships will be made plain in the study of the compounds of thallium which follows, this metal affording one of the most remarkable illustrations of the variation of chemical character with variation of valency.

#### THALLOUS COMPOUNDS

Thallium gradually oxidizes in moist air, when carbon dioxide is absent forming the hydroxide  $\text{TlOH}$ , and when it is present forming the carbonate  $\text{Tl}_2\text{CO}_3$ . On account of this oxidation, the grey mark made by the metal on paper gradually disappears on exposure to air.

**Thalious hydroxide** crystallizes from a strong solution, which may be prepared by acting on a solution of the sulphate with the requisite amount of barium hydroxide, in yellow crystals,  $\text{TlOH}$ ,  $\text{H}_2\text{O}$ , which lose all their water at  $100^\circ$ , leaving thalious oxide,  $\text{Tl}_2\text{O}$ , as a brown powder. The hydroxide is regenerated from the oxide by means of water; its solution in water is strongly alkaline, and absorbs carbon dioxide from the air. In these respects thalious hydroxide resembles the alkali hydroxides; it is, however, less stable than these, as the effect of heating it shows.

**Thalious sulphide**,  $\text{Tl}_2\text{S}$ , differs from the alkali sulphides in

being insoluble in water; it is formed as a black precipitate on passing hydrogen sulphide into a neutral solution of thallous sulphate, but the precipitation is incomplete since the sulphide, like zinc sulphide, is soluble in dilute mineral acids. It is insoluble in alkali-sulphide solutions.

**Halides.**—Thallous fluoride, unlike the other halides, is easily soluble in water, thus resembling silver fluoride, and furnishing another example of the exceptional properties of fluorides. Like potassium fluoride, it readily forms a double fluoride,  $\text{TiHF}_2$ .

The chloride, bromide, and iodide are all formed by precipitation, and stand in order of decreasing solubility. About 1.5 part of the chloride dissolve in 100 parts of boiling water. The chloride is also the product of combustion of thallium in chlorine; like mercurous chloride it is volatile (above  $700^\circ$ ), but the vapour shows the normal density. Thallous chloride is white, and isomorphous with the alkali chlorides, but turns violet on exposure to light, like silver chloride; the bromide is pale yellow and the iodide bright yellow like lead iodide. Thus the halides are closely related to those of Group I B, and also show some analogies with mercurous and lead halides.

**Thallous sulphate**,  $\text{Ti}_2\text{SO}_4$ , closely resembles the alkali sulphates. It is soluble in water and isomorphous with potassium sulphate, and forms an acid sulphate  $\text{TiHSO}_4$ . The most striking analogy, however, is shown in the existence of double salts, such as  $\text{Ti}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ , isomorphous with  $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ , and the alums  $\text{Ti}_2\text{SO}_4 \cdot (\text{Al}_2\text{Fe}_2\text{Cr}_2)(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , which are isomorphous with potassium alum.

It has been shown by Tutton<sup>1</sup> that thallium lies near to rubidium and ammonium, between potassium and caesium, in the isomorphous series of the alkali salts, but that the optical properties of thallous salts do not support this relationship.

**Thallous carbonate**,  $\text{Ti}_2\text{CO}_3$ , is sparingly soluble in water, from which it crystallizes anhydrous; it is more soluble in water containing carbonic acid than in pure water, bicarbonate being formed. In properties thallous carbonate lies between the carbonates of lithium and sodium. The thallous phosphates

<sup>1</sup> *Proc. Roy. Soc.* 79, A, 351.

also show similar relationships as regards solubility, and they are isomorphous with the corresponding potassium compounds;  $\text{Ti}_3\text{PO}_4$  is sparingly soluble,  $\text{Ti}_2\text{HPO}_4$ ,  $\text{H}_2\text{O}$  and  $\text{TiH}_2\text{PO}_4$  are readily soluble in water.

The chlorate  $\text{TiClO}_3$  is sparingly soluble in water; the perchlorate  $\text{TiClO}_4$  and nitrate  $\text{TiNO}_3$  are isomorphous with the corresponding potassium salts. The chromate  $\text{Ti}_2\text{CrO}_4$  is an insoluble yellow powder resembling lead chromate. Hydrochloroplatinic acid,  $\text{H}_2\text{PtCl}_6$ , precipitates the platinichloride  $\text{Ti}_2\text{PtCl}_6$  from solutions of thalious salts.

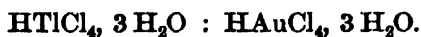
#### THALLIC COMPOUNDS

**Thallic oxide**,  $\text{Ti}_2\text{O}_3$ , although the typical oxide of thallium, is less stable than thalious oxide. It is formed by the combustion of the metal in oxygen, and by the oxidation of thalious oxide by bromine; it is also produced at the anode in the electrolysis of thalious salts. It is a black powder insoluble in water and alkalis, which when heated fuses at  $720^\circ$  and decomposes above  $800^\circ$  into thalious oxide and oxygen. It dissolves to some extent in dilute hydrochloric and sulphuric acids, forming thallic salts, but chlorine and oxygen are readily evolved on warming, especially with the more concentrated acids, thalious salts being formed in solution. In all these respects thallic oxide resembles the group type oxides,  $\text{PbO}_2$  and  $\text{Bi}_2\text{O}_5$ , and thus behaves more as a basic peroxide than a true basic oxide. It differs, however, from the two latter oxides in possessing no acidic properties.

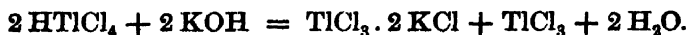
**Thallic hydroxide**,  $\text{Ti}(\text{OH})_3$ , is formed as a brown precipitate when alkalis are added to solutions of thallic salts, or by the hydrolysis of these salts by much water; it is also produced by the oxidation of thalious salts by alkali hypochlorites, and on drying has the composition  $\text{TiOOH}$ . Unlike the other hydroxides of the sub-group, it possesses no acidic properties, being insoluble in alkalis. It is a very weak base, and the thallic salts corresponding to it are generally decomposed by water. The superior acidic properties possessed by aluminium over thallic hydroxide are in

accord with the principles of the periodic law; that thallium is at the same time less electro-positive than aluminium as shown by the relative positions of the two metals in the electro-potential series, shows how widely different the relationships of elements with regard to these two classes of properties may be.

**Thallic chloride**,  $\text{TiCl}_3$ , is the most stable thallic salt. It is formed by the action of chlorine on thallous chloride, and when anhydrous is a crystalline mass melting at  $24^\circ$ .<sup>1</sup> It is soluble in organic solvents and forms compounds with alcohol and ether, as well as crystallizing with water in the forms  $\text{TiCl}_3 \cdot \text{H}_2\text{O}$  and  $\text{TiCl}_3 \cdot 3 \text{H}_2\text{O}$ . It likewise forms with hydrochloric acid the crystalline compound  $\text{TiCl}_3 \cdot \text{HCl} \cdot 3 \text{H}_2\text{O}$ , which is analogous to chlorauric acid, thus:—



Unlike the latter substance, however, chlorothallic acid of the above type does not form alkali salts, for when a solution of this substance is neutralized with potassium hydroxide the following reaction takes place:—



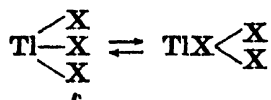
Probably, therefore, the compound  $\text{HTiCl}_4 \cdot 3 \text{H}_2\text{O}$ , which exists in the solid state, is broken up in solution.

In addition to forming double chlorides with the alkali metals, thallic chloride also combines with thallous chloride. Thus when thallium is carefully warmed in chlorine the compound  $\text{TiCl} \cdot \text{TiCl}_3$  or  $\text{TiTlCl}_4$  is formed; this on stronger heating gives  $3 \text{TiCl} \cdot \text{TiCl}_3$ , by which reaction the relative instability of the higher type is shown.

From a nitric-acid solution of thallic chloride the chlorine is not completely precipitated by silver nitrate. This is due to ionisation not proceeding to all the chlorine atoms within the molecule, as in the case of green chromic chloride (*q.v.*). The isomorphism of thallic iodide with rubidium and caesium tri-iodides suggests that thallic halides may possess the

<sup>1</sup> R. J. Meyer, *Zeit. Anorg. Chem.*, xxiv (1900), 321.

constitution  $\text{TlX} \begin{smallmatrix} \text{X} \\ < \\ \text{X} \end{smallmatrix}$ . The instability of the thallic as compared with the thallic type, as well as the resemblance between thallic and alkali salts, make credible the possibility of a transformation such as the following:—



**Thallic sulphate**,  $\text{Tl}_2(\text{SO}_4)_3$ , differs from the allied sulphates of the sub-group in not forming alums. A double sulphate,  $\text{Tl}_2\text{SO}_4 \cdot \text{Tl}_2(\text{SO}_4)_3$ , is known, as well as compounds of the type  $\text{M}_2\text{SO}_4 \cdot \text{Tl}_2(\text{SO}_4)_3 \cdot 8 \text{H}_2\text{O}$ , but these are not true alums.

### SUB-GROUP III A

#### *Scandium, Yttrium, and Lanthanum*

The general relationship of these rare elements to their neighbours of sub-group B is that indicated by the provisions of the periodic law, as is shown here again by the remarkable coincidence in properties between scandium and Mendeléeff's eka-boron.

These metals all display the group valency of three, their oxides and halides being of the types  $\text{M}'''_2\text{O}_3$  and  $\text{M}'''_2\text{X}_3$ . In conformity with the positions assigned to them in the periodic table, they are more positive than the elements of sub-group B, and do not yield volatile organo-metallic compounds or hydrides.

The hydroxides are all basic, being insoluble in the alkali hydroxides, the basic character increasing with rise of atomic weight, so that lanthanum hydroxide is formed directly, with heat evolution, by the hydration of the oxide, and possesses an alkaline reaction, being capable of expelling ammonia from ammonium salts. Yttrium and lanthanum also form stable carbonates by precipitation. The halides of these three elements are non-volatile, and the salts do not suffer extensive hydrolytic dissociation. Double sulphates formed with the alkali metals are not alums.

By fractional precipitation of yttrium salts with ammonia, Crookes has divided yttria into eight components, giving different phosphorescent spectra. Definite chemical differences between these fractions, other than the slight differences in solubility which led to their isolation, cannot be recognized, and what bearing these researches have upon the atomic weight of "yttrium" cannot yet be indicated. In the analogous case of didymium (*q.v.*) more distinct differences have been observed.

## CHAPTER VIII

### GROUP IV

#### SUB-GROUP A

Ti (48.1)  
Zr (90.6)  
Ce (140.25)  

---

Th (232.0)

#### SUB-GROUP B

C (12.00)  
Si (28.3)  

---

Ge (72.5)  
Sn (119.0)  

---

Pb (207.10)

Group IV may be regarded as the transition group, linking the more positive elements of Groups I to III with the more negative elements of Groups V to VII. Consequently the balance between metals and non-metals is more even in this group than in any other, metals predominating in Groups I to III, and non-metals in Groups V to VII. As in most other groups, there is a rise in metallic characters with rise of atomic weight in both sub-groups.

As regards the relationship to each other of the sub-groups A and B, it is to be observed that the respective positions of the analogous elements in the long periods are more nearly alike in this than in any other group. Thus the A members are placed fourth from the commencement, and the B members fourth from the end of these periods, whilst in Group III, for example, the members of the A sub-group are third from the commencement, and those of the B sub-group fifth from the

end, and in Group VII the A member—manganese—is seventh from the commencement, whilst the halogens bromine and iodine are the last members of the long periods.

The relationships indicated by these relative positions of elements in the long periods are borne out by the properties of the elements themselves. Thus the individual members of the sub-groups IV A and IV B, occupying analogous positions, are more nearly related to one another than similarly situated members of any other sub-groups; just as the members of the sub-groups of I and VII are more widely separated in properties than those of any other sub-groups.

As in the other groups, so in Group IV, the members of the A sub-group are more metallic than those of the B sub-group. The members of the B sub-group, together with carbon and silicon, which may appropriately be considered to belong to this sub-group, alone form volatile hydrides and volatile organo-metallic compounds.

The more salient common characteristics of the group are: the display of the maximum valency of four in the hydrides  $MH_4$  and the halides  $MX_4$ ; the formation of typical oxides  $MO_2$ , generally of acidic character; also the combination of the tetrahalides with the corresponding halogen acids and alkali salts to form complex acids and salts, chief among these being the isomorphous complex fluorides of the type  $R_2MF_6$ .

#### SUB-GROUP IV B

##### *Carbon, Silicon, Germanium, Tin, and Lead*

The non-metallic elements, carbon and silicon, are linked by germanium with the more metallic elements tin and lead, just as in Group V B nitrogen and phosphorus are linked by arsenic with antimony and bismuth. The modes of occurrence and extraction of carbon are in many respects exceptional, but the occurrence of silicon in silicates, and its preparation by the reduction of silicifluorides with potassium or aluminium, are characteristic of non-metallic elements, whilst the occurrence and manner of extraction of tin and lead are characteristic rather of metals. Carbon and silicon, moreover, possess

low atomic volumes and high melting-points, display allotropism, and in the amorphous state are bad conductors of heat and electricity; these are characteristics of non-metals, and are not displayed by the higher members of the sub-group. Some of the physical properties of the elements of this sub-group are shown in the following table:—

	C	Si	Ge	Sn	Pb
Atomic weight	12.00	28.3	72.5	119.0	207.10
Density ....	$\left\{ \begin{array}{l} 1.76 \\ \text{amorphous} \\ 2.06 \\ \text{graphite} \\ 3.5 \\ \text{diamond} \end{array} \right\}$	2.35 amorphous	5.47	7.3 (5.85 grey form)	11.34
Melting-point	3600°	?	900°	about 230°	about 330°
Boiling-point	?	—	above 1350°	„ 1500°	1450–1500°

It is to be observed that there is a rise in density on passing from non-metallic carbon to metallic lead, and a fall in melting-point. A comparison of physical properties shows that **carbon** and **silicon** resemble one another in the nature of their allotropic forms. Amorphous silicon is a brown powder which, like amorphous carbon, burns in the air, producing the dioxide, and unites with fluorine at ordinary temperature, forming the tetrafluoride. Silicon unites with chlorine at 450°, and with bromine at 500°, though not directly with iodine; carbon, however, unites directly neither with chlorine, bromine, nor iodine. Carbon and silicon combine together at the temperature of the electric furnace, forming carborundum,  $\text{CSi}$ , an intensely hard substance used for polishing gems. Two other forms of silicon besides the amorphous variety have been described, being known as graphitic and adamantine silicon. The two forms are probably identical with one another, both being obtained by the reduction of silica or a silicifluoride in presence of molten aluminium, from which the silicon crystallizes in black, shining, regular octahedra, isomorphous with diamond. Carbon, however, occurs in two distinctly crystalline forms, graphite and diamond. Graphite is formed when carbon crystallizes from molten iron under atmospheric pressure, diamond being



formed by crystallization from the same solvent by sudden cooling under high pressure. That a difference of pressure chiefly determines which allotropic form is produced is shown by the fact that when diamond is heated to a high temperature under ordinary pressure it is converted into graphite.

Although in the free state carbon resembles silicon, in its compounds its relationship to this and the remaining elements of the group is not so well marked. It is distinguished by the number and stability of its hydrides—the hydrocarbons—the formation of which depends upon the power possessed by carbon atoms of uniting with one another in chains and rings, a phenomenon to which some analogy is presented by silicon, for instance in the compound  $\text{Si}_6\text{Cl}_{14}$ , which probably contains a chain of six silicon atoms. The carbon halides, too, are more stable than those of silicon; and the oxides are gases, whereas those of the other elements of the sub-group are solids, the oxides  $\text{SiO}_2$  and  $\text{SnO}_2$  no doubt possessing high molecular complexity.

The study of carbon compounds will here be limited to such as illustrate analogies or specific differences, valuable for comparative purposes, between this element and other members of the group.

**Germanium** is more metallic in its physical properties than silicon, but shows some resemblance to this element in chemical properties. It burns in the air, forming the dioxide; like silicon, it is insoluble in hydrochloric acid, but soluble in hot caustic alkalis; it, however, resembles tin in forming hydrated dioxide by the action of nitric acid. It forms no volatile hydride, being too metallic.

The elements **tin** and **lead** are of a more pronounced metallic character, both in physical and chemical properties. They form no hydrides; their oxides and halides are less acidic than those of the foregoing elements; and although they maintain some of the characteristics of metalloids, metallic properties predominate.

It will be convenient to study the chief compounds formed by these five elements in one system. There will thus be

presented a view of the changes taking place in various types of compound on passing from distinctly non-metallic to distinctly metallic elements.

#### HYDRIDES (MH<sub>4</sub>)

Carbon and silicon are the only elements of the group which form hydrides, and the above is the chief type common to these two elements.

Methane may be produced by direct synthesis; very small quantities of pure sugar charcoal are converted almost completely into methane when heated in hydrogen at 1150°.¹

Both of these hydrides may be produced by the action of water or acids on suitable carbides or silicides, just as nitrides, phosphides, sulphides, selenides, and tellurides yield the corresponding hydrides.

Aluminium carbide, for instance, yields methane thus:—



and magnesium silicide and hydrochloric acid give the corresponding hydride, silicane,



When ethyl orthosiliciformate,  $\text{SiH}(\text{OC}_2\text{H}_5)_3$ , prepared by the action of ethyl alcohol on silicichloroform, is heated with sodium,² silicane and ethyl orthosilicate result,



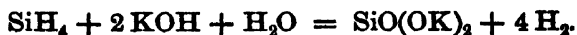
a reaction recalling the behaviour of phosphorous and hypophosphorous acids when heated (*q.v.*). Like methane, silicon hydride or silicane is a gas, which, however, is more easily liquefied than methane. It differs from methane by being spontaneously inflammable³ in air when mixed with hydrogen, or under reduced pressure; behaviour which recalls that of phosphine. It is considerably less stable than methane, being dissociated by heat, and decomposed by potassium hydroxide, yielding potassium silicate and hydrogen,

¹ Zane and Coward, *Chem. Soc. Trans.*, xcvi (1910), 1219.

² The sodium remains unchanged, its rôle in the reaction being unknown.

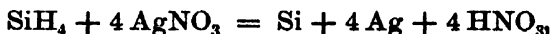
³ As with phosphine, the spontaneous inflammability is due to another hydride present in small quantity, probably  $\text{Si}_2\text{H}_6$ .

a reaction which involves the separation of the hydride into its elements:—

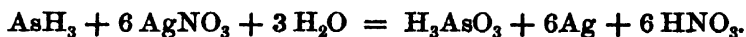


That  $\text{SiH}_4$  should be less stable than  $\text{CH}_4$  is in accordance with the requirement of the periodic law that the stability of gaseous hydrides shall diminish with rise of atomic weight in a group. This point is illustrated by comparing together, as regards stability,  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{AsH}_3$ , and  $\text{SbH}_3$ ,  $\text{BiH}_3$  being unknown, as well as by contrasting  $\text{H}_2\text{O}$  with  $\text{H}_2\text{S}$  and  $\text{HCl}$  with  $\text{HI}$ .

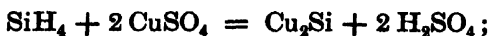
Now unstable hydrides are reducing agents on account of the hydrogen which is liberated in their decomposition. It is true that the hydrides of some of the elements of the fifth group reduce by direct combination with oxygen, but this is due to the oxidizability of the elements themselves; it would hardly be expected, for example, that arsenic would be liberated in the free state by the oxidation of  $\text{AsH}_3$ ; but in the case of  $\text{H}_2\text{S}$  and  $\text{HI}$ , sulphur and iodine are liberated respectively, when the hydrogen with which they are combined is oxidized. The reaction between silicon hydride and silver nitrate, in which silicon and silver are precipitated,



will now be understood, as well as the different behaviour of arsine towards the same reagent,



With less reducible substances, such as copper sulphate, silicides are precipitated,



this reaction being analogous to that with hydrogen sulphide.

Methane possesses no such reactivity as silicane; the only hydrocarbon which possesses analogous properties is acetylene,  $\text{C}_2\text{H}_2$ , which reacts with silver and cuprous compounds, producing acetylides or carbides.

Like methane, silicane undergoes metathesis with chlorine,

and when antimony pentachloride is used as a halogen carrier silici-chloroform,  $\text{SiHCl}_3$ , is formed.

#### OTHER HYDRIDES

Carbon forms many other hydrides, the hydrocarbons, which are generally studied under organic chemistry.

Silicon forms two other hydrides.

**Silico-ethane**,  $\text{Si}_2\text{H}_6$ , a mobile, colourless liquid, boiling at  $52^\circ$ , is among the products of the action of hydrochloric acid on magnesium silicide, prepared by heating magnesium and silicon together.

**Silico-acetylene**,  $(\text{Si}_2\text{H}_2)_n$ , is a stable solid.

#### HALIDES $\text{MX}_4$

The type  $\text{MX}_4$  is characteristic of the group, fluorides, chlorides, bromides, iodides, and mixed halides being known. Of these the fluorides and chlorides, since they are known for each element,<sup>1</sup> afford the best comparative data.

#### FLUORIDES

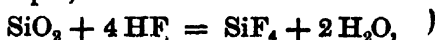
$\text{CF}_4$ gas	$\text{SiF}_4$ gas	$\text{GeF}_4$ solid + 3 $\text{H}_2\text{O}$	$\text{SnF}_4$ in aqueous solution	$\text{PbF}_4$ yellow powder.
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#### CHLORIDES

$\text{CCl}_4$ liquid B.P. $76^\circ$	$\text{SiCl}_4$ liquid B.P. $59.6^\circ$	$\text{GeCl}_4$ liquid B.P. $86^\circ$	$\text{SnCl}_4$ liquid B.P. $113.9^\circ$	$\text{PbCl}_4$ liquid decomposed by heat.
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The **tetrafluorides** are formed by the direct union of the elements, and **carbon tetrafluoride**, the only carbon halide formed in this way, has been thus prepared.

(They are generally obtained, however, by the action of hydrofluoric acid, derived from  $\text{CaF}_2$  and  $\text{H}_2\text{SO}_4$ , upon the dioxides, for example,



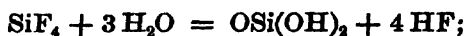
or the corresponding alkali salts, stannates and plumbates, in which case the alkali double fluorides result, *e.g.*



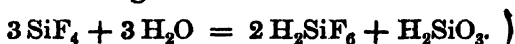
<sup>1</sup>  $\text{SnF}_4$  is known only in aqueous solution and  $\text{GeF}_4$  as a crystallohydrate.

from which the fluorides themselves are separated by concentrated sulphuric acid. )

The halanhydride character of silicon tetrafluoride is shown by its reaction with water, when silicic and hydrofluoric acids are formed,



the hydrofluoric acid, however, combines with more silicon tetrafluoride, producing the stable hydrofluosilicic acid,<sup>1</sup> the complete reaction being:



Of the tetrachlorides, that of carbon is not formed by direct union, but results as the final chlorine substitution product of methane or carbon disulphide; all the other elements, however, unite directly with chlorine, the compounds  $\text{SiCl}_4$ ,  $\text{GeCl}_4$ , and  $\text{SnCl}_4$  being thus prepared.

Silicon tetrachloride also results from the action of chlorine on a heated mixture of carbon and silicon dioxide,



whilst germanium and tin tetrachlorides are formed by distilling together the metal and mercuric chloride. Lead tetrachloride is produced in solution when chlorine is passed through hydrochloric acid in which lead dichloride is suspended. Ammonium plumbichloride,  $(\text{NH}_4)_2\text{PbCl}_6$ , is precipitated from this solution on adding ammonium chloride, and when this salt is decomposed by cold concentrated sulphuric acid,  $\text{PbCl}_4$  separates as an unstable liquid.

The distinguishing characteristic of the tetrachlorides is that they are chloranhydrides rather than salts; thus they are volatile liquids, whilst typical salts are relatively non-volatile solids; they are unacted on by cold concentrated sulphuric acid, and, whilst soluble in non-hydroxylic solvents, do not dissolve without change in water, but are decomposed by it, or by alkalis, with formation of the acidic hydroxides  $\text{M(OH)}_4$ , or  $\text{OM(OH)}_2$ , or their salts.

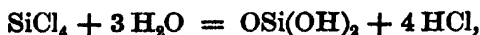
<sup>1</sup> Boron trifluoride (g.v.) combines similarly with HF.

**Carbon tetrachloride** presents an anomalous character, being, like the hydride, comparatively inert; it is insoluble in, and not acted on by, water, but the prolonged action of potassium hydroxide gives carbonate and chloride,



a reaction which reveals the relationship of carbon tetrachloride to carbonic acid.

✓Silicon tetrachloride is at once decomposed by water, giving silicic and hydrochloric acids,



but the chlorides  $\text{SnCl}_4$  and  $\text{PbCl}_4$  are capable of forming crystallohydrates, those of tin containing from three to nine molecules of water. The chlorides  $\text{SnCl}_4$ ,  $\text{GeCl}_4$ , and  $\text{PbCl}_4$  are moderately stable in aqueous solution when an excess of hydrochloric acid is present, but in dilute solution, and in the absence of much hydrochloric acid, they are decomposed like silicon tetrachloride. ✕

Various double halides of the type  $\text{R}_2\text{MX}_6$ , derived from the acids  $\text{H}_2\text{MX}_6$ , are known in the case of the elements of Group IV B, as well as of IV A, some of which have been referred to in the preceding paragraphs. Of these the best known are the fluorides, though chlorides and bromides, but not iodides, exist. Carbon forms no such compounds on account of the inertness of its halides, and silicon forms only fluorides, that is  $\text{H}_2\text{SiF}_6$  and its salts. Tin and lead, as well as thorium, the most metallic elements of the group, form double chlorides such as are not formed by the more non-metallic elements.

#### OXYCHLORIDES

Just as chlorides or chloranhydrides of the type  $\text{MCl}_4$  are the chlorides of the ortho-acids  $\text{M(OH)}_4$ , so oxychlorides of the type  $\text{MOCl}_2$  are the chlorides of the meta-acids  $\text{MO(OH)}_2$ .

**Carbonyl chloride**,  $\text{COCl}_2$ , known as phosgene gas, is formed by the union of carbon monoxide and chlorine. It boils at  $8^\circ$ , is decomposed by water into  $\text{CO}_2$  and  $\text{HCl}$ , after the manner

of acid chlorides, and reacts with ammonia, forming carbamide or urea,  $\text{CO}(\text{NH}_2)_2$ .

The analogous silicyl chloride is not known.  $\text{Si}_2\text{OCl}_6$ , however, formed when  $\text{SiCl}_4$  exchanges some chlorine for oxygen at high temperature, is a fuming liquid, boiling at  $137^\circ$ , and easily decomposed into silicic and hydrochloric acids.

$\text{SnOCl}_2$  results from the oxidation of  $\text{SnCl}_2$ ;  $\text{PbOCl}_2$  is unknown.

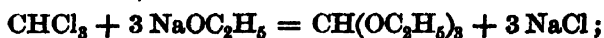
#### DERIVATIVES OF THE TYPE $\text{MHX}_3$

Trihalide derivatives of the hydrides  $\text{CH}_4$  and  $\text{SiH}_4$  are analogous, and germanium, although forming no hydride, forms the trichloride  $\text{GeHCl}_3$ . Since  $\text{CHCl}_3$ , the chloranhydride of orthoformic acid,  $\text{CH}(\text{OH})_3$ , is known as chloroform, the analogous silicon and germanium compounds, as well as the bromine and iodine derivatives, receive similar names. The following substances of the type  $\text{MHX}_3$  are known,<sup>1</sup> and are formed when the elements are heated in a stream of hydrogen halide gas.

	C	Si	Ge
$\text{M HCl}_3$ .....	chloroform $\text{CHCl}_3$ B.P. $61^\circ$	silicichloroform $\text{SiHCl}_3$ B.P. $34^\circ$	germanichloroform $\text{GeHCl}_3$ B.P. $72^\circ$
$\text{M HBr}_3$ .....	bromoform $\text{CHBr}_3$ B.P. $151^\circ$	silicibromoform $\text{SiHBr}_3$ B.P. about $115^\circ$	?
$\text{M HI}_3$ .....	iodoform $\text{CHI}_3$ M.P. $119^\circ$	siliciiodoform $\text{SiHI}_3$ B.P. $220^\circ$	?

It will be seen that, as in the case of the tetrahalides, the boiling-points of the silicon compounds are consistently lower than those of the corresponding carbon compounds, but that with germanium the boiling-points of the compounds rise again.

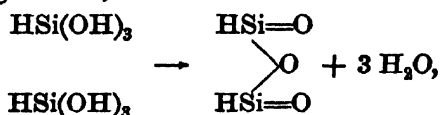
Just as  $\text{CHCl}_3$  corresponds with  $\text{CH}(\text{OH})_3$ , the hypothetical orthoformic acid, into derivatives of which it is converted by sodium alcoholates, thus:—



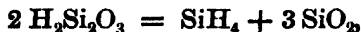
<sup>1</sup> Silicifluoroform,  $\text{SiHF}_3$ , likewise exists as a colourless gas, condensing at  $-80^\circ$ .

so **silicichloroform**,  $\text{SiHCl}_3$ , corresponds with  $\text{SiH}(\text{OH})_3$  and its alkyl compounds. Thus alcohol itself, without the use of sodium, forms ethyl orthosiliciformate,  $\text{SiH}(\text{OC}_2\text{H}_5)_3$ , a change which shows  $\text{SiHCl}_3$  to be more reactive than  $\text{CHCl}_3$ , just as  $\text{SiCl}_4$  is more reactive than  $\text{CCl}_4$ .

Silicichloroform also is slowly hydrolysed by water, which does not decompose chloroform, the product being **leucone**, or orthosiliciformic acid,  $\text{SiH}(\text{OH})_3$ ; the corresponding carbon compound does not exist. Leucone is, however, rather unstable, easily losing water; thus:—



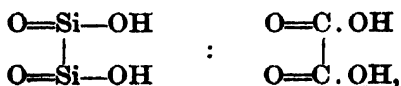
the resulting product being known as siliciformic anhydride. It is, however, a neutral substance which is broken up by heat into silicon, hydrogen, and silicon dioxide, a reaction probably preceded by the formation of  $\text{SiH}_4$ ,



the hydride then decomposing thus,  $\text{SiH}_4 = \text{Si} + 2 \text{H}_2$ .

When comparing together the elements carbon and silicon, it was pointed out that whilst no silicon derivatives corresponding to the paraffin hydrocarbons exist, beyond silicane, certain chlorine analogues of unknown hydrosilicons are known. These are  $\text{Si}_2\text{Cl}_6$ ,  $\text{Si}_3\text{Cl}_8$ ,  $\text{Si}_4\text{Cl}_{10}$ , and  $\text{Si}_5\text{Cl}_{14}$ .<sup>1</sup> The two former compounds are among those obtained when chlorine is passed over a heated mixture of magnesium and silica, and are separated from the tetrachloride and from each other by fractional distillation. They are fuming liquids;  $\text{Si}_2\text{Cl}_6$  boils at  $146\text{--}148^\circ$ ,  $\text{Si}_3\text{Cl}_8$  at  $210\text{--}215^\circ$ ; the analogous carbon compounds  $\text{C}_2\text{Cl}_6$  and  $\text{C}_3\text{Cl}_8$  boil at  $185^\circ$  and  $268\text{--}269^\circ$  (734 mm.) respectively.

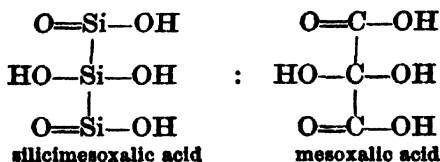
$\text{Si}_2\text{Cl}_6$  is hydrolysed by water, producing silicioxalic acid, analogous to oxalic acid;



<sup>1</sup> Besson and Fournier, *Compt. rend.* (1909), 148, 839, 149, 34.



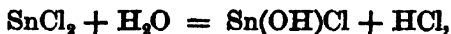
and  $\text{Si}_2\text{Cl}_6$ , under similar conditions, gives silicimesoxalic acid:



#### HALIDES $\text{MX}_2$

Halides of the type  $\text{MX}_2$  are unknown with carbon and silicon, but are represented in the case of germanium, tin, and lead. Little is known of germanious halides, but stannous and lead halides are important compounds which manifest definite saline characters, being prepared by the methods usually available for the formation of salts, for example, in the case of tin, by the action of the halogen acid on the metal, as well as by its action on the monoxides in the case of tin and lead, and by precipitation of salts of the latter metal, whose halides are but slightly soluble in water.

Chloranhydride characters are manifested slightly by stannous chloride, but scarcely at all by lead chloride. For example, stannous chloride is somewhat soluble in ether, whilst lead chloride is insoluble, and stannous chloride melts at a lower temperature than lead chloride; also, whilst stannous chloride is decomposed by excess of water according to the reaction,



lead chloride is not so decomposed, although basic salts are formed by combination with  $\text{PbO}$ . Both chlorides form double salts with alkali chlorides, the chief of which correspond to the acid type  $\text{H}_2\text{MCl}_4$ ; the acid  $\text{H}_2\text{SnCl}_4$ , as well as  $\text{HSnCl}_3$  probably exists in a solution of stannous chloride in hydrochloric acid. Lead chloride, bromide, and iodide show progressive insolubility in cold water, in which they resemble mercuric and silver halides; they are, however, easily soluble in hot water, differing in this respect from the silver halides and mercuric iodide.

OXIDES OF THE TYPE  $\text{MO}_2$ 

These, corresponding to the maximum oxygen valency of the group, are known for each element.  $\text{CO}_2$ ,  $\text{SiO}_2$ ,  $\text{GeO}_2$ , and  $\text{SnO}_2$  are the products of the direct union of the elements with oxygen, and  $\text{GeO}_2$  and  $\text{SnO}_2$  are formed by the action of nitric acid on the elements;  $\text{CO}_2$ ,  $\text{SiO}_2$ , and  $\text{SnO}_2$  occur naturally in the free state, and  $\text{CO}_2$  and  $\text{SiO}_2$  combined in the form of carbonates and silicates.  $\text{PbO}_2$  is not the most stable oxide of lead, being obtained, not by the combustion of the metal, but by the oxidation of the monoxide, *e.g.* by hypochlorite solution,  $\text{PbO} + \text{NaOCl} = \text{PbO}_2 + \text{NaCl}$ ; and being reconverted into the monoxide by heat.

A comparison of the physical properties of these oxides reveals a great contrast between gaseous carbon dioxide on the one hand, and on the other solid silica, existing in the amorphous and two crystalline forms of quartz and tridymite, together with the solid dioxides of germanium, tin, and lead. The melting-point of silica is very high; it can, however, be melted, and even vaporized, in the electric furnace. Molten silica may be worked like glass, and made into tubes or flasks, which are useful because, on account of the minute coefficient of expansion of the substance, they are not fractured by sudden changes of temperature.

Inasmuch as the chlorides of silicon are more volatile than the corresponding carbon compounds, this great difference in properties between  $\text{CO}_2$  and  $\text{SiO}_2$  must be attributed to the polymerisation of the latter substance, which in all its known forms exists in very complex molecules.

Each of these oxides is acidic, giving rise to a weak acid of the type  $\text{M}(\text{OH})_4$  or  $\text{MO}(\text{OH})_2$ ; lead dioxide, however, must be regarded also as a basic peroxide, since although with alkali hydroxides plumbates such as  $\text{K}_2\text{PbO}_3$  are formed, the action of acids produces salts corresponding to the basic oxide  $\text{PbO}$ , oxygen or its equivalent being set free.<sup>1</sup> In this respect lead is analogous to its neighbour in series, bismuth, whose pentoxide behaves as a basic peroxide as well as a feebly acidic oxide.

<sup>1</sup> The tetra-acetate  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_4$ , however, exists.

## ORTHO-ACIDS

Of the ortho-acids,  $M(OH)_4$ , **orthosilicic acid**,  $H_4SiO_4$ , may exist in solution, and **orthostannic acid**,  $H_4SnO_4$ , can be precipitated by alkali hydroxide from a solution of stannic chloride, or by the hydrolysis of ammonium stannate caused by boiling; the others are unknown. Organic orthocarbonates are represented by  $C(OC_2H_5)_4$ , orthosilicates by  $Si(OC_2H_5)_4$ , and the minerals olivine,  $Mg_2SiO_4$ , and zircon,  $ZrSiO_4$ ; red-lead,  $Pb_3O_4(Pb_2PbO_4)$ , may also be referred to the same type, since  $PbO_2$  is separated from it by nitric acid. No orthostannates are known, but calcium orthoplumbate,  $Ca_2PbO_4$ , occurs crystalline.

## META-ACIDS

Meta-acids of the type  $MO(OH)_2$  are represented by **carbonic acid**,  $H_2CO_3$ , which exists in dilute aqueous solution; **metasilicic acid**,  $H_2SiO_3$ , which is approximately the composition of air-dried "gelatinous silica" precipitated from a strong solution of an alkali silicate by acid; so-called  $\alpha$ -stannic acid, better known as  **$\alpha$ -metastannic acid**,  $H_2SnO_3$ , similarly obtained from a stannate by the action of an acid, or by the decomposition of stannic chloride by water in presence of calcium carbonate; and  $H_2PbO_3$ , which is deposited at the anode in the electrolysis of an alkaline solution of a lead salt.

Of the salts derived from the meta-acids,  $MO(OH)_2$ , the **carbonates**, really metacarbonates, are well known; the alkali **metasilicates**, such as  $Na_2SiO_3$ , are supposed to exist in "soluble glass", the mass obtained by fusing silica with an alkali carbonate, and also occur in nature in definite crystalline compounds, such as Wollastonite,  $CaSiO_3$ ; the **metastannates**,  $K_2SnO_3$  and  $Na_2SnO_3$ , commonly known as  $\alpha$ -stannates, are obtained by evaporating the solution of the hydrated dioxide in alkali hydroxide, in well-defined crystals containing  $3 H_2O$ . Potassium **metaplumbate**,  $K_2PbO_3 \cdot 2 H_2O$ , is a crystalline salt.  $Pb_2O_3$  is lead metaplumbate,  $PbPbO_3$ ; from each of these compounds lead dioxide is separated by acid. The salts of these acids are easily hydrolysed by water or dilute mineral acids,

because the acids themselves are very weak; when the acids are separated by hydrolysis they readily break up into the anhydrides and water, as in the case of carbonic acid, or yield partially hydrated and complex dehydration products.

Ammonium silicate, like the corresponding stannate, is hydrolysed by water, and this fact accounts for the separation of gelatinous silica when ammonium carbonate or other ammonium salt is added to a solution of a silicate; thus:—



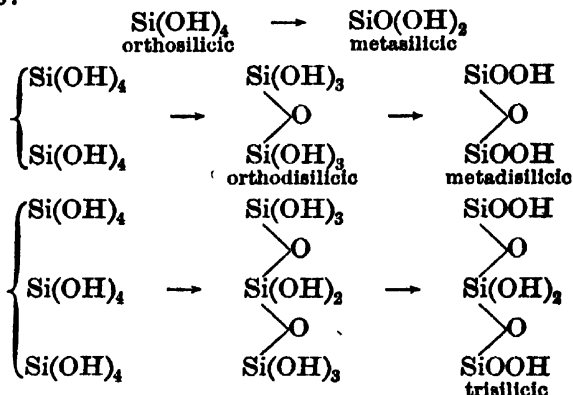
Freshly precipitated silicic acid, corresponding approximately to the formula  $\text{H}_2\text{SiO}_3$ , is appreciably soluble in water and dilute acids; it loses water at  $100^\circ$ ,  $\text{H}_2\text{Si}_2\text{O}_5$ , insoluble in water and acids, being formed; and by further heating bodies containing less and less water are obtained, until eventually anhydrous silica remains. By loss of water, hydrated silica becomes less soluble in alkali carbonate and hydroxide solutions.

When acid is added to a dilute solution of sodium silicate, no precipitate is formed, the silicic acid forming a colloidal suspension. The difference between this behaviour and that of a more concentrated solution is not solely dependent on concentration, but upon the existence of the hydrated silica in the colloidal state in the former case, when it enters into molecular union with the water, forming a complex which may be represented by the formula  $(\text{SiO}_2)_n(2 \text{H}_2\text{O})_m$ , where  $m$  is slightly less than  $n$ , rather than by the simpler formula  $\text{SiO}_2, 2 \text{H}_2\text{O}$ . This state persists when the solution is dialysed, so that a concentrated *hydrosol* is formed, which easily yields a gelatinous precipitate of *hydrogel*.

As a weak acid, silicic acid also forms salts of great complexity, so that the types of metallic silicates are numerous; other feeble acids show a similar tendency, for instance, boric, tungstic, molybdic, and chromic acids.

Most of the metallic silicates fall into classes corresponding with the following silicic acids: orthosilicic  $\text{H}_4\text{SiO}_4$ , metasilicic  $\text{H}_2\text{SiO}_3$ , disilicic  $\text{H}_2\text{Si}_2\text{O}_5$ , and trisilicic  $\text{H}_4\text{Si}_3\text{O}_8$ , and basic silicates derived from ortho and metasilicic acids.

The various silicic acids may all be formulated as partial dehydration products of one or more molecules of orthosilicic acid; thus:—



Some representatives of the orthosilicic class are:

Olivine  $\text{Mg}_2\text{SiO}_4$ , Zircon  $\text{ZrSiO}_4$ , Garnet  $\text{Al}_2\text{Ca}_3(\text{SiO}_4)_3$ .

Of the metasilicic class,

Wollastonite  $\text{CaSiO}_3$ , Augite  $\text{CaMg}(\text{SiO}_3)_2$ , Talc  $\text{H}_2\text{Mg}_3(\text{SiO}_3)_4$ ,  
Emerald  $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ .

Of the trisilicic class,

Felspar  $(\text{K}, \text{Na})\text{AlSi}_3\text{O}_8$ .

Of basic silicates,

Andalusite  $\text{Al(AlO)SiO}_4$ .

In addition to these, there are numerous hydrated silicates, containing water of crystallization, easily expelled on heating, and which, as a rule, are attacked by hydrochloric acid.

An analogy may be drawn between silicates and alloys. When silica and basic oxides are fused together, an amorphous slag or glass is formed, from which on cooling under favourable conditions crystalline silicates may separate, just as crystalline compounds of the metals may under like conditions be obtained from the molten alloy. The silicates, like alloys, may be regarded as loose compounds of the components, lying on the border line between the definite chemical compound and the mixture.

Various complex stannic acids and their salts are known.

In addition to the true metastannic acid, generally known as  $\alpha$ -stannic acid, which was mentioned above, a polymer, generally called metastannic acid but better described as  $\beta$ -metastannic acid, and to which the composition  $(\text{H}_2\text{SnO}_3)_5$  is assigned, is formed by the action of moderately concentrated nitric acid on tin. Stannic nitrate is probably first produced, but being unstable decomposes into oxides of nitrogen and an insoluble cream-white powder having the above composition.

$\beta$ -metastannic acid, whose formula may be written  $\text{Sn}_5\text{O}_5(\text{OH})_{10}$ , and whose potassium salt is  $\text{Sn}_5\text{O}_5(\text{OK})_2(\text{OH})_8$ , when acted on by hydrochloric acid, gives rise to  $\beta$ -stannyl chlorides such as  $\text{Sn}_5\text{O}_5\text{Cl}_2(\text{OH})_8$  and  $\text{Sn}_5\text{O}_5\text{Cl}_4(\text{OH})_6$ , which are reconverted into the acid by excess of water. The compound  $\text{Sn}_5\text{O}_5\text{Cl}_2(\text{OH})_8$ , which is soluble in water, gives a precipitate of  $\beta$ -stannyl sulphate with potassium sulphate or sulphuric-acid solution. Prolonged action of hydrochloric acid on  $\beta$ -metastannic acid produces stannic chloride,  $\text{SnCl}_4$ , and concentrated potassium-hydroxide solution similarly forms potassium  $\alpha$ -metastannate,  $\text{K}_2\text{SnO}_3$ ; the ten-membered ring  $(\text{Sn}_5\text{O}_5)$ , which probably forms the nucleus of these polymeric varieties of metastannic acid, being broken down by such treatment.

Thus stannic oxide resembles silica in being the parent substance of various complex acids and salts, though it differs from it in possessing distinctly basic properties; stannic acid, like silicic acid, can also exist in the colloidal state, but such a condition is very unstable.

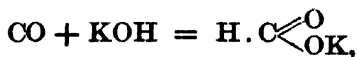
#### OXIDES OF THE TYPE MO AND THEIR DERIVATIVES

The type MO is represented by the oxides  $\text{CO}$ ,  $\text{GeO}$ ,  $\text{SnO}$ , and  $\text{PbO}$ <sup>1</sup>. CO is generally regarded as a neutral oxide, GeO is little known, SnO and PbO are somewhat feebly basic oxides, whose hydroxides  $\text{Sn}(\text{OH})_2$  and  $\text{Pb}(\text{OH})_2$  are obtained from

<sup>1</sup> Silicon forms no monoxide, but, according to Simmonds (*Chem. Soc. Trans.* lxxxv (1904), 681), the reduction by hydrogen of such a silicate as that of lead yields some "silicite" corresponding to the oxide SiO.

their salts by precipitation. As might be expected, these salts show a tendency to be hydrolysed by water, giving rise to basic salts. The hydroxides also exhibit acid properties by reason of their solubility in excess of alkali hydroxide solutions.

**Carbon Monoxide.**—The relationship of carbon monoxide to formic acid is interesting. Although carbon monoxide does not yield that acid with water, it is gradually absorbed by strong potassium hydroxide, producing potassium formate,



and might therefore be considered the anhydride of formic acid, especially also as it is obtained when the acid is dehydrated by means of sulphuric acid. An inspection of the constitution of the oxide and acid shows, however, that formic acid is not hydroxylated carbon monoxide, which would be  $\text{C} \begin{array}{c} \text{OH} \\ \diagup \\ \text{OH} \end{array}$ ; thus combination of the oxide with potassium hydroxide involves a molecular rearrangement, as is shown in the above equation. Only in a limited and unusual sense, then, can carbon monoxide be considered the anhydride of formic acid.

**Stannous oxide**,  $\text{SnO}$ , is a black powder, obtained by igniting the hydroxide out of contact with air; its formation may sometimes be observed during the action of cold dilute nitric acid on tin.

The hydroxide  $\text{Sn}(\text{OH})_2$ , formed as a white precipitate by the addition of alkali hydroxide or carbonate solution to a solution of a stannous salt, dissolves in excess of alkali hydroxide, forming a stannite,  $\text{Sn}(\text{OM}')_2$ ; thus it exhibits both basic and acidic properties like alumina. **Stannous sulphate** and **nitrate** are formed by the action of the dilute acids on tin or stannous hydroxide, and are very easily hydrolysed by water. Stannous carbonate is unknown.

**Lead monoxide**,  $\text{PbO}$ , known as litharge or massicot, is the most stable oxide of lead, resulting when either of the other oxides is ignited strongly in air. It is fusible and may be obtained crystalline. The hydroxide  $\text{Pb}(\text{OH})_2$  is slightly

soluble in water, to which it imparts an alkaline reaction. It is formed in solution when water containing dissolved oxygen acts on metallic lead. In spite of the basic properties indicated by its alkaline reaction, lead hydroxide, when precipitated from a lead salt by alkali hydroxide, dissolves in excess of the reagent, producing plumbite,  $\text{Pb}(\text{OM}')_2$ .

Since lead is more basigenic than tin, its oxysalts, derived from  $\text{PbO}$ , are more stable than the stannous oxysalts. **Lead sulphate**,  $\text{PbSO}_4$ , is nearly insoluble in water; consequently the action of dilute sulphuric acid on lead, with the evolution of hydrogen, is soon arrested by the formation of a crust of sulphate upon the metal; lead, however, dissolves in warm, concentrated sulphuric acid, forming an acid sulphate, thus:—



this salt is hydrolysed by water,  $\text{PbSO}_4$  being precipitated. In its insolubility in water and its solubility in concentrated sulphuric acid, as well as by reason of isomorphism, this salt closely resembles barium sulphate. **Lead nitrate**,  $\text{Pb}(\text{NO}_3)_2$ , formed by dissolving the metal or the oxide in nitric acid, crystallizes in regular octahedra, isomorphous with barium nitrate. Its aqueous solution shows but a faintly acid reaction; basic salts, such as  $\text{Pb}(\text{OH})\text{NO}_3$ , are formed when the solution is digested with lead monoxide. (A further resemblance between lead and barium is shown in the properties of the chromates, both of which are yellow solids insoluble in water and acetic acid. This resemblance, however, does not extend to chemical properties; it is not generic, as the hydrolysis and solution of lead chromate by potassium hydroxide, owing to the acidic properties of lead hydroxide, whilst barium chromate is insoluble in this reagent, is sufficient to indicate. It may here be pointed out that no true conclusion as to the relationships between elements can be drawn from a consideration of the physical properties of their compounds alone. The chemical differences between barium and lead and their compounds require the elements to be placed in different categories, apart altogether from the indications of

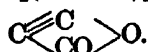


the periodic law. At the same time physical relationships are not to be ignored, though what precise significance is to be attached to them in the present case cannot be said.)

**Lead carbonate**,  $\text{PbCO}_3$ , is precipitated when alkali-bicarbonate solution is added to a lead salt, a basic carbonate resulting when the normal carbonate solution is used. White-lead is the basic carbonate,  $2\text{PbCO}_3, \text{Pb(OH)}_2$ . The native form of lead carbonate, cerussite, is isomorphous with barium carbonate, but except for their insolubility in water, there is no further resemblance between the two salts, since barium carbonate does not easily lose carbon dioxide when heated nor form a basic salt, as does lead carbonate. Tin being less basigenic than lead, forms no carbonate.

#### SUB- AND PEROXIDES

The gaseous oxide of carbon,  $\text{C}_3\text{O}_2$ ,<sup>1</sup> is a dehydration product of malonic acid,  $\text{CH}_2(\text{COOH})_2$ , and probably possesses the constitution



★ Lead forms a suboxide,  $\text{Pb}_2\text{O}$ , which is the first product of the oxidation of lead, and is obtained as a black powder when lead oxalate is heated out of contact with oxygen:



When heated, this oxide decomposes into lead and monoxide.

Tin forms a hydrated peroxide,  $2\text{SnO}_3, \text{H}_2\text{O}$ , or  $\text{H}_2\text{Sn}_2\text{O}_7$ , which is produced when barium peroxide is added to a solution of stannous chloride in dilute hydrochloric acid, and remains in colloidal suspension after dialysis.

#### SULPHIDES

The sulphides of the group resemble the oxides in chemical properties. The more important are  $\text{CS}_2$ —together with  $\text{COS}$ , — $\text{SnS}$ ,  $\text{SnS}_2$ , and  $\text{PbS}$ . A gradation of properties may be observed in these sulphides similar to that which obtains in the oxides, though, as in other groups, the sulphides are distinctly less acidic than the corresponding oxides. Carbon and tin disulphides dissolve in alkali sulphide solutions,

<sup>1</sup> Ber. 1906, 39, 689 and 1915.

forming thiocarbonates and thio-stannates respectively. With alkali hydroxides, mixtures of thio- and oxy-salts result, or salts of the oxyacids in which oxygen is partially replaced by sulphur. Lead sulphide is insoluble in alkali hydroxides and sulphides, which fact, considering that lead hydroxide is soluble in potassium-hydroxide solution, illustrates the more feebly acidic character of the sulphide. The difference of behaviour of lead and tin sulphides towards alkalis serves to separate the metals in analysis.

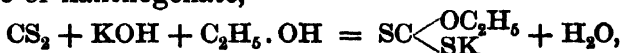
Carbon disulphide,  $\text{CS}_2$ , boils at  $46^\circ$  under atmospheric pressure, the boiling-point of  $\text{CO}_2$  being  $-78^\circ$ . As thiocarbonic anhydride, carbon disulphide might give rise to two acids, orthothiocarbonic acid,  $\text{H}_4\text{CS}_4$ , and metathiocarbonic acid,  $\text{H}_2\text{CS}_3$ , and their salts. Salts of both acids exist, though those of the meta-acid are the more important. The meta-acid is known in the free state, and is produced as an unstable reddish oil, when an aqueous solution of sodium metathiocarbonate, formed by dissolving carbon disulphide in sodium-sulphide solution, is acidified. In accordance with the feebler character of the thio- as compared with the oxy-salts, sodium metathiocarbonate is decomposed by carbon dioxide; thus:—



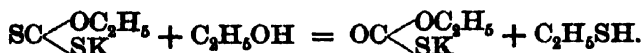
and even by excess of water, with formation of carbonate and  $\text{H}_2\text{S}$ :—



With alcoholic potassium hydroxide,  $\text{CS}_2$  yields potassium xanthate or xanthogenate,



from which the acid itself  $\text{SC} \cdot \text{OC}_2\text{H}_5 \cdot \text{SH}$  is separated as an unstable oil on acidifying; whereas by the action of excess of alcoholic potash, a sulphur atom is removed, and potassium ethyl monothiocarbonate results,

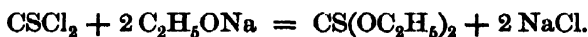


Isomeric with the unknown, unsymmetrical dithiocarbonic

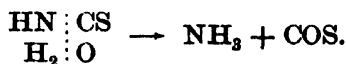
acid,  $\text{SC} \begin{smallmatrix} \text{OH} \\ \text{SH} \end{smallmatrix}$ , of which xanthic acid is the ethyl ester, is the symmetrical acid  $\text{OC} \begin{smallmatrix} \text{SH} \\ \text{SH} \end{smallmatrix}$ , whose ethyl ester results from the action of sodium ethyl sulphide on carbonyl chloride:



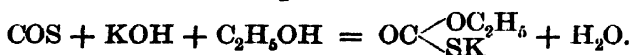
similarly the isomer of the above monothiocarbonic acid  $\text{OC} \begin{smallmatrix} \text{OH} \\ \text{SH} \end{smallmatrix}$ , namely  $\text{SC} \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix}$ , is represented in the form of its ethyl salt, prepared by the action of sodium ethoxide on thiocarbonyl chloride:



The gas, **carbon oxysulphide**, or carbonyl sulphide, results from the direct union of carbon monoxide and sulphur at high temperature, also from the hydrolysis of thiocyanic acid, liberated from its salts, by dilute sulphuric acid.



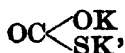
The oxysulphide dissolves in alcoholic potassium-hydroxide solution, forming potassium ethyl monothiocarbonate, in a manner entirely analogous to that by which xanthates are produced from carbon disulphide:—



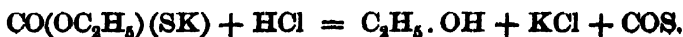
When aqueous potassium-hydroxide solution is used, potassium carbonate and sulphide are formed; thus:—



the wholly metallic monothiocarbonate,



which might be expected, not being formed. Similarly the oxysulphide is slowly decomposed by water into  $\text{CO}_2$  and  $\text{H}_2\text{S}$ . From ethyl monothiocarbonate, hydrochloric acid liberates the oxysulphide, thus:—



**Stannous sulphide**,  $\text{SnS}$ , a dark-brown powder, insoluble in water, is decomposed by concentrated hydrochloric acid,

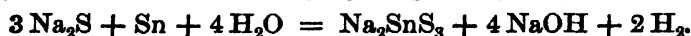


the metallic properties of tin are thus manifested, since less metallic sulphides such as arsenious sulphide,  $\text{As}_2\text{S}_3$ , are not attacked by this reagent.<sup>1</sup>

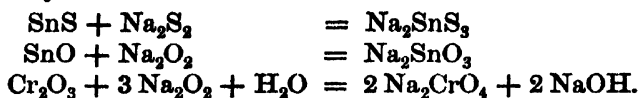
Stannous sulphide is soluble with some difficulty in sodium-hydroxide solution, even when the precipitate is finely divided; the following reaction takes place:—



$\text{SnS}$  is practically insoluble in dilute sodium-sulphide solution, but a concentrated solution of this reagent gradually decomposes it into  $\text{SnS}_2$  and  $\text{Sn}$ , the former of which dissolves readily, and the latter slowly, giving off hydrogen, thus:—



Stannous sulphide easily dissolves in alkali polysulphides, including yellow ammonium sulphide, forming thiostannate, just as stannous oxide and chromic oxide dissolve in sodium-peroxide solution, forming sodium stannate and chromate respectively:

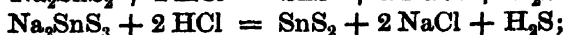
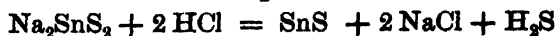


**Stannic sulphide**,  $\text{SnS}_2$ , prepared by subliming a mixture of tin, sulphur, and ammonium chloride, is known as mosaic gold; when precipitated it is a dull-yellow powder, which generally contains some hydrated dioxide. It dissolves easily in alkali sulphide and hydroxide solutions, thus showing superior acidic properties to  $\text{SnS}$ , and forming thiostannate and a mixture of stannate and thiostannate respectively.

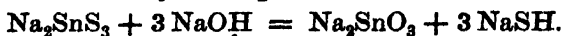
Metathiostannic acid,  $\text{H}_2\text{SnS}_3$ , and its alkali salts exist in the solid state, and an orthosalt of the composition  $\text{Na}_4\text{SnS}_4 \cdot 12\text{H}_2\text{O}$  has been prepared.

<sup>1</sup> With this may be compared the different behaviour of non-metallic and metallic chlorides towards sulphuric acid.

Acids decompose thioannites and thioannates, reprecipitating stannous or stannic sulphide:



whilst alkalis convert them, as they do thiocarbonates, into oxyalts and alkali hydrosulphide:



This reaction illustrates the superior stability and acidity of the oxides over the sulphides.

#### SUB-GROUP IV A

##### *Titanium, Zirconium, Cerium, and Thorium*

The elements of sub-group IV A, titanium, zirconium, cerium, and thorium, are more metallic than those of the B sub-group, and the metallic properties increase with rise of atomic weight in accordance with the requirements of the periodic law. As, however, was pointed out in the introduction to this group, the differences between analogous members of the sub-groups are less in this than in any other group. The types of compounds formed by these elements are more numerous than in sub-group B.

The following **oxides** are known:—

	Ti	Zr	Ce	Th
M <sub>2</sub> O <sub>2</sub> .....	Ti <sub>2</sub> O <sub>2</sub>	—	—	—
M <sub>2</sub> O <sub>3</sub> .....	Ti <sub>2</sub> O <sub>3</sub>	—	Ce <sub>2</sub> O <sub>3</sub>	—
MO <sub>3</sub> .....	TiO <sub>2</sub>	ZrO <sub>2</sub>	CeO <sub>2</sub>	ThO <sub>2</sub>
M <sub>2</sub> O <sub>5</sub> .....	—	Zr <sub>2</sub> O <sub>5</sub>	—	—
MO <sub>3</sub> .....	TiO <sub>3</sub>	ZrO <sub>3</sub>	CeO <sub>3</sub>	—
M <sub>2</sub> O <sub>7</sub> .....	—	—	—	Th <sub>2</sub> O <sub>7</sub>

#### HYDROXIDES CORRESPONDING TO THE TYPICAL OXIDES

These are precipitated from the corresponding salt solutions by alkali hydroxide. Ti(OH)<sub>4</sub> is almost insoluble, and the other hydroxides are quite insoluble in excess of alkali, so that acidic properties are almost absent from the typical oxides of this group. Rutile, TiO<sub>2</sub>, which is isomorphous with SnO<sub>2</sub>, yields the titanate K<sub>2</sub>TiO<sub>3</sub> by fusion, a salt which is completely hydrolysed by water. **Titanium hydroxide, Ti(OH)<sub>4</sub>,**

when precipitated from cold solutions, is readily soluble in acids;  $\text{TiO}(\text{OH})_2$ , which is formed from hot solutions, is soluble in acids with much difficulty, and is therefore, probably, polymeric, like  $\beta$ -metastannic acid. A solution of  $\text{TiCl}_4$  in water probably contains colloidal titanic acid, from which the insoluble form separates on long heating.

**Zirconium hydroxides**,  $\text{Zr}(\text{OH})_4$  and  $\text{ZrO}(\text{OH})_2$ , closely resemble those of titanium, except that they are completely insoluble in alkali-hydroxide solution. Alkali zirconates, formed by fusion, are completely hydrolysed by water, but the hydroxide, like cupric hydroxide, tenaciously retains alkali.

**Ceric hydroxide** easily forms a colloidal suspension with water; and when ceric-nitrate solution is evaporated to a syrup on the water bath, and the residue is dissolved in water, a yellow precipitate of basic ceric nitrate is formed on the addition of a drop of nitric acid. This is due to the change of the basic salt from the *hydrosol* to the *hydrogel* form by the action of acid.

**Thorium hydroxide**,  $\text{Th}(\text{OH})_4$ , is a stable substance, forming  $\text{ThO}_2$  by loss of water on ignition, the intermediate meta-compound  $\text{ThO}(\text{OH})_2$  not being formed. Thoria, with about one per cent of ceria,  $\text{CeO}_2$ , constitutes the material of the mantle of incandescent gas light.

#### HALIDES $\text{MX}_4$

The halides show a transition of properties with rise of atomic weight, signifying a change from feebly- to well-developed metallic characters in the elements.

The fluorides of the elements of a group often show exceptional properties when compared with the other halides. These properties are, in the case of non-metals, the power to form stable complex acids by combination with hydrofluoric acid, an example of which is seen in hydrofluosilicic acid,  $\text{H}_2\text{SiF}_6$ , and in the case of metals, great differences of solubility, as shown in the case of the alkaline-earth fluorides, when compared with the corresponding chlorides. Both these peculiarities are observable in the fluorides of this sub-group.

**Titanium tetrafluoride**,  $\text{TiF}_4$ , is a liquid which with water gives hydrofluotitanic acid,  $\text{H}_2\text{TiF}_6$ , and titanic oxyfluoride. The alkali titanifluorides, or fluotitanates, are stable salts isomorphous with the corresponding silici-, germani-, and stannifluorides.

**Zirconium tetrafluoride**,  $\text{ZrF}_4$ , is sparingly soluble in, and not hydrolysed by water;  $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$  can be crystallized from dilute hydrofluoric acid solution. The zirconifluorides are well-defined salts, isomorphous with the other complex fluorides of the group, whilst the zirconichlorides are not formed in the wet way (*cf.* titanichlorides).

**Cerium tetrafluoride**,  $\text{CeF}_4$ , forms double salts, but not of the usual type; when heated, it decomposes into  $\text{CeF}_3$  and fluorine gas.

**Thorium tetrafluoride**,  $\text{ThF}_4$ ,  $4\text{H}_2\text{O}$ , is formed as a gelatinous precipitate when an alkali fluoride is added to a solution of a thorium salt. Thorifluorides also exist.

Of the **chlorides**,  $\text{TiCl}_4$  alone is a liquid, boiling at  $136^\circ$ ; it is apparently soluble in water, producing probably colloidal suspension of titanic acid. A solution of  $\text{TiCl}_4$  in hydrochloric acid contains  $\text{H}_2\text{TiCl}_6$ , and from this solution, on addition of ammonium chloride, a yellow crystalline precipitate of  $(\text{NH}_4)_2\text{TiCl}_6 \cdot 2\text{H}_2\text{O}$  is obtained by shaking.  $\text{ZrCl}_4$  is crystalline and volatile, and gives with water the oxychloride  $\text{ZrOCl}_2$ ; it thus resembles  $\text{BiCl}_3$  in saline character.  $\text{CeCl}_4$  is very unstable,  $\text{CeCl}_3$  and chlorine being obtained when  $\text{CeO}_2$  is dissolved in hydrochloric acid.

$\text{ThCl}_4$  sublimes when chlorine is passed over a heated mixture of  $\text{ThO}_2$  and carbon. It forms crystallohydrates with water and double salts with alkali chlorides.

#### OXYSALTS CORRESPONDING TO THE TYPICAL OXIDES

**Titanic sulphate**,  $\text{Ti}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ , exists, and forms the double salt,  $\text{K}_2\text{SO}_4 \cdot \text{Ti}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ , as well as the basic salt,  $\text{TiOSO}_4$ ; the carbonate and nitrate do not exist, and the sulphide is not formed in the wet way; indeed all titanic salts are completely hydrolysed by water.

**Zirconium sulphate**,  $\text{Zr}(\text{SO}_4)_2$ , is produced when the hydroxide is dissolved in sulphuric acid. It forms basic salts, and leaves a residue of zirconia on strong ignition. An unstable nitrate exists, and a basic carbonate, but the sulphide is not formed in the wet way.

The ceric salts are orange-red; **ceric sulphate**,  $\text{Ce}(\text{SO}_4)_2$ , is soluble in and forms crystallohydrates with water, as well as basic salts. The nitrate is hydrolysed by water, and decomposed by heat, but forms stable double salts with alkali nitrates; the carbonate is known.

**Thorium sulphate** and **nitrate** are well-defined soluble salts which are little hydrolysed by water. The aqueous solution of the sulphate  $\text{Th}(\text{SO}_4)_2$  forms several crystallohydrates, separating at different temperatures, and also double salts with alkali sulphates. The basic carbonate, obtained by precipitation by alkali-carbonate solution, dissolves in excess of the precipitant, forming a double salt. The sulphide is not formed by precipitation in the wet way.

#### DERIVATIVES OF LOWER OXIDES

**Titanious chloride**,  $\text{TiCl}_3$ , is obtained from  $\text{TiCl}_4$  by reduction with hydrogen. It consists of violet scales which form with water a violet, strongly reducing solution.<sup>1</sup> When heated, this salt decomposes into volatile  $\text{TiCl}_4$  and non-volatile  $\text{TiCl}_2$ , to which the oxide  $\text{Ti}_2\text{O}_3$  corresponds. Alkalis precipitate  $\text{Ti}(\text{OH})_3$ ;  $\text{Ti}_2\text{O}_3$ , which results from heating  $\text{TiO}_2$  in a current of hydrogen, is more basic than the latter oxide, and forms a well-defined **sulphate**, yielding rubidium and caesium alums. Zirconium and thorium form no lower oxides, but **cerous oxide**,  $\text{Ce}_2\text{O}_3$ , and its salts are important, especially as in these compounds cerium is related to the earth metals, both as regards natural occurrence<sup>2</sup> and in the properties of the salts.

**Cerous chloride**,  $\text{CeCl}_3$ , is a yellowish-white, volatile, stable substance forming crystallohydrates; the **sulphate**,  $\text{Ce}_2(\text{SO}_4)_3$ ,

<sup>1</sup> On this account  $\text{TiCl}_3$  is used for the volumetric estimation of ferric iron, organic nitro compounds, &c. *Vide* Knecht and Hibbert's *New Reduction Methods in Volumetric Analysis*.

<sup>2</sup> Cerite, gadolinite, and samarskite contain  $\text{Ce}_2\text{O}_3$ ,  $\text{Di}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ , together with other basic oxides and silica; monazite is  $(\text{Ce}, \text{La}, \text{Di})\text{PO}_4$ , and lanthanite  $(\text{CeLa})_2(\text{CO}_3)_3$ .



also forms several crystallohydrates, as well as double sulphates with the alkali sulphates, the salt  $\text{Ce}_2(\text{SO}_4)_3, 3 \text{K}_2\text{SO}_4$  closely resembling the corresponding lanthanum and didymium compounds. The crystalline nitrate,  $\text{Ce}(\text{NO}_3)_3, 6 \text{H}_2\text{O}$ , and the normal carbonate,  $\text{Ce}_2(\text{CO}_3)_3, 5 \text{H}_2\text{O}$ , exist. It will be seen from these facts that the titanious and cerous are distinctly more saline than the titanio and ceric compounds, into which they are respectively converted by oxidizing agents.

### PEROXIDES

**Titanium peroxide**,  $\text{TiO}_2$ , is obtained in a hydrated condition as a yellow powder, when ammonia is added to an alcoholic solution of  $\text{TiCl}_4$  to which hydrogen peroxide has been added. This compound is to be regarded as a superoxide which is acidic rather than basic, for its alkali and alkaline-earth salts are known, and when potassium fluoride is added to its solution in hydrochloric acid, potassium titanifluoride,  $\text{K}_2\text{TiF}_6$ , is precipitated, and hydrogen peroxide is formed in solution.

**Zirconium peroxide**,  $\text{ZrO}_2$ , is produced in a similar manner, and forms perzirconates with the alkalis.  $\text{Zr}_2\text{O}_5, 9 \text{H}_2\text{O}$  is said also to be formed as a white powder when hydrogen peroxide is added to a solution of zirconium sulphate. The **peroxides of cerium and thorium**,  $\text{CeO}_3$  and  $\text{Th}_2\text{O}_7$ —the existence of  $\text{ThO}_3$  is doubtful—are formed by means of hydrogen peroxide, like the foregoing, and are basic superoxides.

## CHAPTER IX

### GROUP V

SUB-GROUP A	SUB-GROUP B
	N (14.01)
	P (31.04)
V (51.06)	As (74.96)
Nb (Cb) (93.5)	Sb (120.2)
[Di] Pr (140.6)	—
Nd (144.3)	
Ta (181.0)	Bi (208.0)

Nitrogen, the first "typical" element of this group, presents more pronounced oxygenic characters than are met with in any of the preceding groups. For instance, whilst the acids formed by the oxides of carbon and silicon are weak, nitric acid is among the strongest acids.

Diminution of the acidic character of analogous compounds takes place from phosphorus to bismuth in sub-group B; and, in accordance with previously recognized principles, the elements vanadium, niobium, didymium, and tantalum, of the A sub-group, are relatively the more basigenic.

## SUB-GROUP VB

The ability to form stable, gaseous hydrides is a characteristic of non-metals, and the transition from non-metal to metal in the elements of this group is well shown in the properties of the hydrides, the stability of which diminishes from nitrogen through phosphorus and arsenic to antimony; whilst no hydride of bismuth has been isolated. The heats of formation, which are a measure of relative chemical stability, together with the temperature of rapid decomposition of these hydrides, are given in the following table:—

	Heat of Formation.		Temperature of Rapid Decomposition.
NH <sub>3</sub> .....	118.9 K	.....	1300°
PH <sub>3</sub> .....	36.6 K	.....	?
AsH <sub>3</sub> .....	—11.7 K	.....	230°
SbH <sub>3</sub> .....	—84.5 K	.....	150°

With the oxygenic properties of the elements themselves are associated basic or salt-forming properties in their hydrides, as is seen by comparing together ammonium and phosphonium compounds. The solution of ammonia in water is alkaline, and therefore contains ammonium hydroxide, NH<sub>4</sub>OH, which has undergone a certain amount of electrolytic dissociation; phosphine, however, is only slightly soluble in water, forming a neutral solution, which probably does not contain any phosphonium hydroxide.

Phosphonium salts, too, are far less stable than those of

ammonium; only the halides, and possibly the sulphate, are known, and these are at once decomposed by cold water with the evolution of phosphine; in the case of ammonium salts, an analogous hydrolytic decomposition only takes place slowly on boiling with water. The hydrides of arsenic and antimony do not form salts.

It might be supposed that basic properties of the hydrides would increase from nitrogen to antimony since the elements themselves become more basigenic. The formation of salts analogous to those of ammonium depends, however, upon the power of developing pentavalency possessed by the element rather than upon basigenic or metallic properties; moreover, a fourth hydrogen atom is one of the elements to be taken up, and power to combine with hydrogen in such manner is not possessed by metals.

Whilst, therefore, arsenic and antimony manifest pentavalency towards oxygen, they cannot combine with more than three hydrogen atoms; and the trihydrides even are rather unstable. Thus the manifestation of basic properties by hydrides, which among all the elements is practically confined to nitrogen, depends upon the possession of non-metallic characteristics by the element, which enable it to take up another atom of hydrogen, together with a negative radicle, when it becomes pentavalent.

The base-forming properties of this class of compound are increased by the exchange of hydrogen atoms for alkyl groups. This is a general rule, which is illustrated likewise by derivatives of sulphur and selenium. Tetra-alkylammonium hydroxides, formed by the action of moist silver oxide on their halides, are analogous in properties to sodium and potassium hydroxides, and possess a strongly alkaline reaction. Tetra-alkylphosphonium salts are much more stable than the simple phosphonium compounds, and they yield the hydroxides by treatment with moist silver oxide. The same is true of tetra-alkylarsonium and stibonium compounds. Bismuth alkyls exist, but they do not possess basic properties.

Passing from the B to the A sub-group, it is found that none

SUMMARY OF SUB-GROUP V<sup>B</sup>

Progs. of Element.	N	P	As	Sb	Bi
At. Wt. ....	14.01	31.04	74.96	120.2	208.0
Density .....	solid { at -195.5 = 8042 }	P <sub>4</sub> 1.88, P <sub>2</sub> 2.10	{ Δαα 3.88, Δαβ 4.71 }	6.62	9.78
M.P. ....	at -259.5 = -1.0355 }	P <sub>4</sub> 44.1	Asγ 5.73	432°	285°
B.P. ....	-214°	290°	500° high press	1450°	above 1000°
Hydrides .....	NH <sub>3</sub> , N <sub>2</sub> H <sub>4</sub> , N <sub>2</sub> H <sub>2</sub> ? N <sub>2</sub> H	PH <sub>3</sub> , P <sub>2</sub> H <sub>4</sub> (P <sub>2</sub> H) <sub>2</sub>	AsH <sub>3</sub> , As <sub>2</sub> H <sub>4</sub>	SbH <sub>3</sub>	—
Oxides X <sub>2</sub> O .....	N <sub>2</sub> O	—	As <sub>2</sub> O <sub>3</sub> ?	—	—
X <sub>2</sub> O <sub>3</sub> .....	NO	—	—	—	Bi <sub>2</sub> O <sub>3</sub> ?
X <sub>2</sub> O <sub>4</sub> .....	N <sub>2</sub> O <sub>3</sub> ⇌ NO + NO <sub>2</sub>	P <sub>2</sub> O <sub>6</sub>	As <sub>2</sub> O <sub>6</sub>	Sb <sub>2</sub> O <sub>6</sub>	Bi <sub>2</sub> O <sub>6</sub>
X <sub>2</sub> O <sub>5</sub> .....	N <sub>2</sub> O <sub>4</sub> ⇌ 2NO <sub>2</sub>	P <sub>2</sub> O <sub>4</sub>	—	Sb <sub>2</sub> O <sub>4</sub>	Bi <sub>2</sub> O <sub>4</sub>
X <sub>2</sub> O <sub>6</sub> .....	N <sub>2</sub> O <sub>5</sub> ⇌ 2NO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	As <sub>2</sub> O <sub>5</sub>	Sb <sub>2</sub> O <sub>5</sub>	Bi <sub>2</sub> O <sub>5</sub>
Hydroxides X(OH) <sub>3</sub> .....	N <sub>2</sub> (OH) <sub>2</sub>	[H <sub>3</sub> POOH]	—	—	—
{ XO.OH, X <sub>2</sub> O(OH) <sub>2</sub> .....	N <sub>2</sub> (OH) <sub>2</sub>	PO.OH	{ AsO.ONa <sup>+</sup> }	{ SbO.ONa <sup>+</sup> }	—
X(OH) <sub>3</sub> .....	NO.OH	P(OH) <sub>3</sub> ⇌ HPO(OH) <sub>2</sub>	{ As <sub>2</sub> O.(ONa) <sub>4</sub> }	{ Sb <sub>2</sub> O.(OH) <sub>4</sub> }	—
X <sub>2</sub> O(OH) <sub>4</sub> .....	—	P <sub>2</sub> O <sub>4</sub> (OH) <sub>4</sub>	AsOAg <sub>3</sub>	Sb(OH) <sub>3</sub>	Bi(OH) <sub>3</sub>
X <sub>2</sub> O(OH) <sub>5</sub> .....	—	—	—	Sb <sub>2</sub> O <sub>4</sub> (ONa) <sub>2</sub>	—
XO.OH .....	NO <sub>2</sub> .OH	PO <sub>2</sub> .OH	AsO <sub>3</sub> .OH	SbO <sub>3</sub> .OH	BiO <sub>3</sub> .OH
X <sub>2</sub> O(OH) <sub>4</sub> .....	—	P <sub>2</sub> O <sub>4</sub> (OH) <sub>4</sub>	As <sub>2</sub> O <sub>4</sub> (OH) <sub>4</sub>	Sb <sub>2</sub> O <sub>4</sub> (OH) <sub>4</sub>	—
X <sub>2</sub> O(OH) <sub>5</sub> .....	—	PO(OH) <sub>2</sub>	AsO(OH) <sub>3</sub>	SbO(OH) <sub>3</sub>	—
X(OH) <sub>3</sub> .....	—	—	—	—	—
Chlorides—					
XCl <sub>3</sub> .....	—	PCl <sub>3</sub>	—	SbCl <sub>3</sub> , SbOCl	BiCl <sub>3</sub>
XCl <sub>4</sub> .....	NOCl	PCl <sub>4</sub> , POCl <sub>3</sub>	AsCl <sub>3</sub> , As(OH) <sub>2</sub> Cl	—	BiCl <sub>3</sub> , BiOCl
XCl <sub>5</sub> , XOCl <sub>3</sub> .....	—	—	—	SbCl <sub>5</sub>	—

\* Where the acid itself is unknown the sodium or other salt is given.

of the elements of the latter group form gaseous hydrides. This is consistent with what has previously been observed; namely, that members of sub-groups A form neither volatile hydrides nor volatile organo-metallic compounds.

By reference to the synoptic table on the previous page, it will be seen that numerous oxygen compounds are known belonging to a number of different types. In a general study of the oxides or hydroxides of any group two considerations must be borne in mind: (i) the diminution of oxygenic properties with increasing atomic weight, these persisting longer in the B than in the A sub-groups; (ii) the enhancing of these properties in a particular element by the addition of oxygen. Thus, for example, (i) taking the type  $R_2O_5$ , the acidic properties diminish in the series  $N_2O_5$ ,  $P_2O_5$ ,  $As_2O_5$ ,  $Sb_2O_5$ ,  $Bi_2O_5$ , from member to member, and (ii) considering the series  $NH_4OH \rightarrow N(OH)_5$ , the latter of which is represented in a meta form by  $NO_2 \cdot OH$ , the properties of the compounds change from those of a weak base to those of a powerful acid.

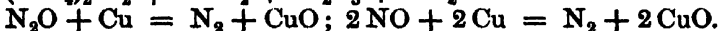
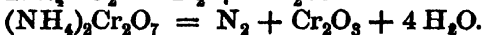
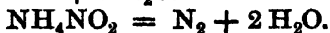
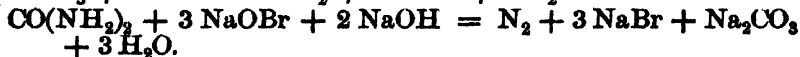
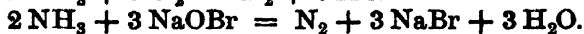
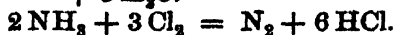
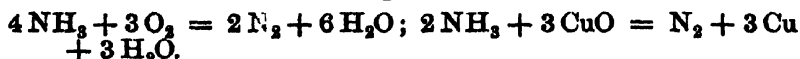
Inasmuch as nitrogen and phosphorus possess strong individuality and form some types of compounds which are unrepresented among the other members of the group, it will be convenient to study them separately. Arsenic, antimony, and bismuth will then be compared with one another and with phosphorus, and finally the members of the A sub-group will be briefly considered.

## NITROGEN

The atmosphere is the chief storehouse of nitrogen; thus the greater part of this element on our planet exists in the free state. This fact may be attributed to the inertness of nitrogen; that is, the difficulty with which it combines with other elements.

The subject of the fixation and circulation of nitrogen will be dealt with at the end of this chapter; here it may be noted that the methods for preparing nitrogen artificially consist either in the oxidation of ammonia and its derivatives, or in the reduction of oxides of nitrogen.

This is shown in the following reactions:—



#### HYDRIDES OF NITROGEN

Nitrogen forms the following compounds with hydrogen:—

$\text{NH}_3$  Ammonia,

$\text{N}_2\text{H}_4$  Diamide or Hydrazine,

$\text{N}_2\text{H}_2$  Di-imide (existence doubtful),

$\text{N}_3\text{H}$  Azoimide or Hydrazoic acid.

This series of compounds shows a transition from basic to acidic properties, with a decrease in the proportion of hydrogen.  $\text{N}_3\text{H}$  is more acidic than  $\text{SH}_2$ , and is comparable with the hydracids of the seventh group, the complex  $\text{N}_3$  being analogous to a halogen atom. Increase in acidity with loss of hydrogen is a general phenomenon well illustrated in certain carbon compounds, for instance, the series:—



the last only of these compounds, acetylene, behaving as an acid, its hydrogen atoms being replaceable by metals.

**Ammonia,  $\text{NH}_3$ .**—Of this substance little need be said, its methods of preparation and properties being well known.

One or more of the hydrogen atoms of  $\text{NH}_3$  may be replaced by different elements or radicles, the nature of the resulting compound depending on the properties of the substituting atom or group. The alkali metals produce compounds of the type  $\text{NH}_2\text{M}$ , *e.g.* sodamide,  $\text{NH}_2\text{Na}$ , which on contact with water breaks up into ammonia and sodium hydroxide. Sodium hypochlorite yields chloramine,  $\text{NH}_2\text{Cl}$ , an unstable oil giving with alkalis  $\text{NH}_3$  and  $\text{N}_2$ . Hydrocarbon radicles may replace one, two, or three atoms of hydrogen, producing respectively



Hydrazine likewise results from the oxidation of ammonia in solution by sodium hypochlorite, the liquid being made viscous with glue; and also from the oxidation of urea by the same reagent.<sup>1</sup> The latter reaction is essentially  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH}_2 + \text{O} = \text{NH}_2 \cdot \text{NH}_2 + \text{CO}_2$ , reached through a series of intermediate reactions, the further oxidation of the hydrazine being prevented by the presence of benzaldehyde, with which hydrazine forms the insoluble compound benzalazine,  $\text{C}_6\text{H}_5\text{CH:N:N:CH} \cdot \text{C}_6\text{H}_5$ .

An aqueous solution of hydrazine, prepared by distilling a salt with alkali, is alkaline, and probably contains the dihydrate,  $\text{HO} \cdot \text{NH}_2 \cdot \text{NH}_2 \cdot \text{OH}$ . The monohydrate is obtained on evaporation as a highly refractive liquid, slightly heavier than water, boiling at  $118.5^\circ$ , and remaining liquid at  $-40^\circ$ . It may be described as hydrazonium hydroxide,  $\text{NH}_2 \cdot \text{NH}_2 \cdot \text{OH}$ .

Pure hydrazine was obtained by Lobry de Bruyn by treatment of the hydrate with anhydrous baryta and distillation under reduced pressure, and is a hygroscopic liquid, boiling at  $113.5^\circ$  under ordinary pressure, and solidifying at  $1.4^\circ$ . It reacts vigorously with water, forming the monohydrate, and decomposes when heated thus:  $3 \text{N}_2\text{H}_4 = \text{N}_2 + 4 \text{NH}_3$ .

Hydrazine is a powerful reducing agent, precipitating silver, mercury, and gold from their solutions at atmospheric temperature. Fehling's solution also is easily reduced. The reaction is essentially  $\text{N}_2\text{H}_4 + 2 \text{O} = \text{N}_2 + 2 \text{H}_2\text{O}$ , nitrogen being evolved. Azoimide,  $\text{N}_3\text{H}$ , results from the oxidation of hydrazine by hydrogen peroxide and sulphuric acid.

Hydrazine forms two hydrochlorides,  $\text{N}_2\text{H}_4 \cdot \text{HCl}$  and  $\text{N}_2\text{H}_4 \cdot 2 \text{HCl}$ ; both salts are easily soluble in water.

The dihydrochloride melts at  $198^\circ$ , losing  $\text{HCl}$ , and forming the monohydrochloride, which melts at  $89^\circ$ .

The sulphate,  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ , is sparingly soluble in water.

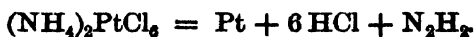
Although hydrazine has only comparatively recently been isolated, its substitution compounds, particularly phenylhydrazine,  $\text{C}_6\text{H}_5 \cdot \text{NHNH}_2$ , were known previously. The formation of hydrazides,  $\text{R} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$ , and hydrazones,  $\text{R}_2\text{C} : \text{N} \cdot \text{NH}_2$ ,

<sup>1</sup> Schestakoff, *J. Russ. Phys. Chem. Soc.*, 1906, 37, 1.



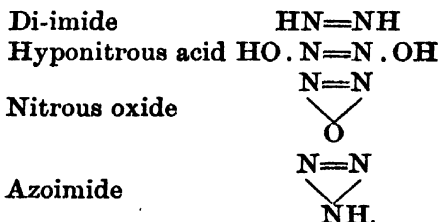
by hydrazine and its derivatives, are valuable reactions in the study of the carbon compounds.

**Di-imide,  $N_2H_2$ .**—Little is known of this substance. It is said to be a gas formed by the decomposition of ammonium chloroplatinate by heat:

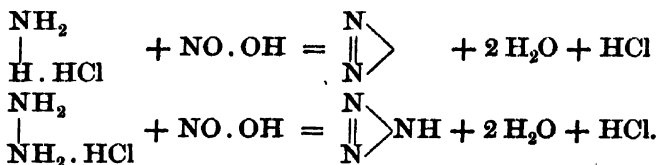


**Azoimide or Hydrazoic acid,  $N_3H$ .**

The following substances contain the azo grouping,  $-N=N-$ :

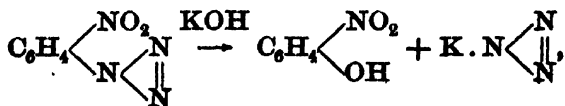


Azoimide may be obtained by the action of nitrous acid on salts of hydrazine. This method of preparation is analogous to that by which nitrogen is obtained from ammonium salts:



The substance was first obtained, however, by Curtius from hippuryl hydrazine ( $C_6H_5CO.NH.CH_2.CO.NH.NH_2$ ) by an analogous reaction, the hippurylazoimide produced being hydrolysed by dilute acid or alkali.

Paranitrophenylazoimide, formed together with other substances by the action of ordinary strong nitric acid on phenylazoimide, yields the alkali salt of azoimide by hydrolysis:—



and from the alkali salt, azoimide itself can be obtained by distillation with dilute sulphuric acid.

(W. Wislicenus prepared azoimide by the action of nitrous oxide on sodamide thus:—

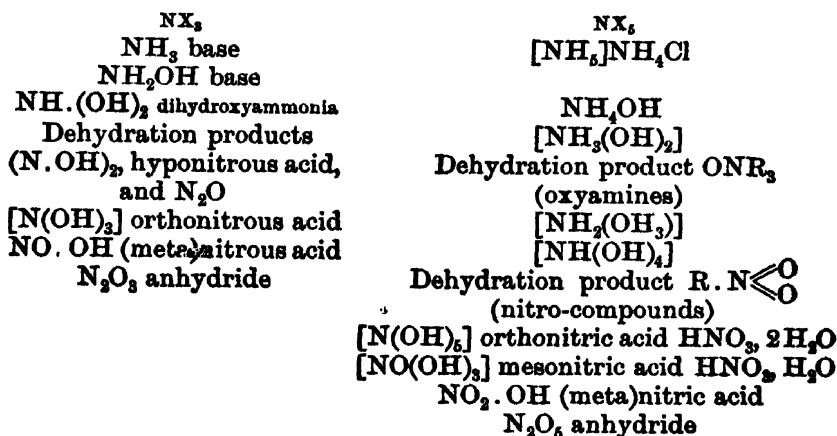


the sodium salt being decomposed by sulphuric acid and the acid obtained by distillation. )

Pure azoimide, obtained by distilling the potassium salt with dilute sulphuric acid, and condensing the dried vapours by means of liquid air, is a mobile liquid with a penetrating smell, boiling at  $30^\circ$ , freezing at  $-80^\circ$ , and highly explosive. A dilute aqueous solution has an acid reaction, having undergone electrolytic dissociation to the extent of about 1 per cent. This substance is therefore known as hydrazoic acid, and its salts as hydrazoates, azides, or simply nitrides. The silver, mercurous, and lead salts are sparingly soluble in water, thus resembling the corresponding halides. Like the acid itself, they are explosive.

#### CLASSIFICATION OF CERTAIN NITROGEN COMPOUNDS

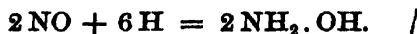
The various classes of compounds containing a single nitrogen atom may be advantageously summarized according to the following scheme, which shows the various stages of oxidation:—



Compounds in square brackets are unknown.

NX<sub>3</sub> TYPE

(**Hydroxylamine**,  $\text{NH}_2 \cdot \text{OH}$  (oxyammonia), was discovered in 1865 by Lossen, who obtained it by the action of nascent hydrogen on nitric oxide:



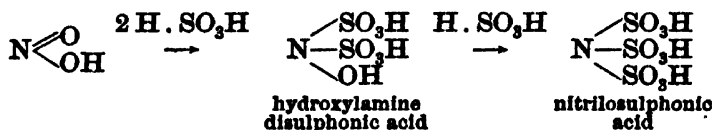
It is also formed by the reduction of nitric acid, by tin or zinc, and may be produced and identified by the following simple experiment:—

“Pour some dilute sulphuric acid on zinc, and then a little nitric acid, when the effervescence will lessen to a marked extent; in half a minute pour off the acid solution and add potash in large excess to dissolve the zinc hydroxide; then add a little very dilute copper-sulphate solution. A yellow precipitate of hydrated cuprous oxide will be produced.”<sup>1</sup> This reaction may be represented by the following equation:—

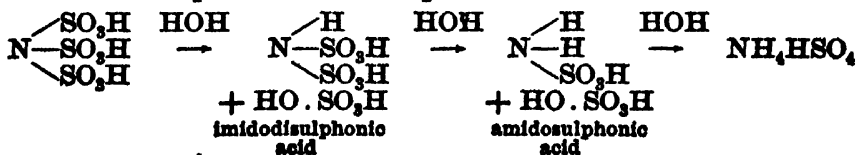


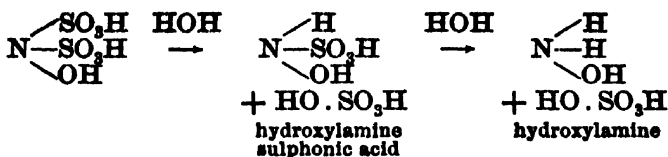
Hydroxylamine may also be obtained by the reduction of nitroparaffins, such as  $\text{CH}_3 \cdot \text{NO}_2$ , but the most important method for the production of this substance consists in the sulphonation of nitrous acid by sulphurous acid and the hydrolytic reduction of the product. †

The following scheme represents the mechanism of the sulphonation of nitrous acid:—

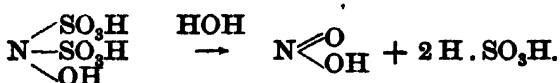


The hydrolysis of these two products may be effected in two ways. If water or dilute acid is used there is reduction with simultaneous production of sulphuric acid:

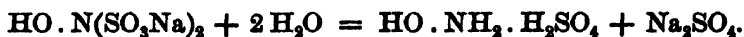




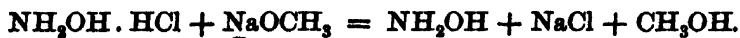
Hydrolysis by alkalis does not involve reduction, and sulphite is regenerated:



According to Divers, normal sulphites do not react with alkali nitrites. Nitrous and sulphurous acids react, but the presence of base is necessary to combine with the products and render them stable. Thus the alkali salts of hydroxylamine disulphonic and nitrilosulphonic acids may be obtained, and when the former are boiled with dilute acids, salts of hydroxylamine are produced:

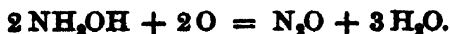


Pure anhydrous hydroxylamine was prepared in 1891 by Lobry de Bruyn, by bringing together hydroxylamine hydrochloride and sodium methoxide in methyl-alcoholic solution, sodium chloride being precipitated:

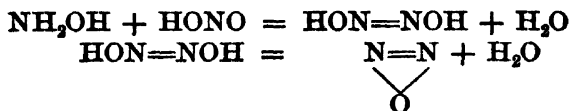


The hydroxylamine was fractionated under reduced pressure, after distilling off the methyl alcohol, and obtained as a white crystalline solid, melting at  $30^\circ$  and boiling at  $70^\circ$  under 60 mm. pressure. Crismer obtained it in the same year by distilling  $\text{ZnCl}_2 \cdot 2 \text{NH}_2\text{OH}$ .

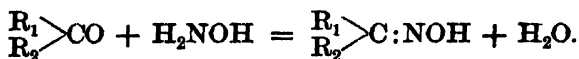
An aqueous solution of hydroxylamine is alkaline, but unstable, soon breaking up into nitrogen, ammonia, and water. It reduces copper, mercury, silver, and gold solutions, and decolorizes iodine, nitrous oxide being produced in these reactions thus:—



Hydroxylamine reacts with nitrous acid, first producing hyponitrous acid and then nitrous oxide:—

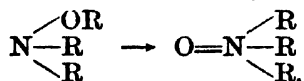


Hydroxylamine is employed for the preparation of oximes, which are formed from aldehydes and ketones according to the reaction:—



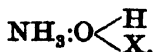
It is chiefly known in the form of its crystalline salts, such as the hydrochloride, sulphate, and nitrate, which are more stable than the free base.

Mono- and di- substituted hydroxylamines,  $\text{NHR}_1 \cdot \text{OH}$  and  $\text{NR}_1\text{R}_2 \cdot \text{OH}$  exist, but the displacement of the third hydrogen atom results in the formation of an oxyamine,<sup>1</sup> thus:—



Oxyamines, which are bases, may likewise be obtained by the action of hydrogen peroxide on tri-substituted amines,  $\text{NR}_3$ .

Ebler and Schott<sup>2</sup> believe hydroxylamine itself to be tautomeric, thus:  $\text{NH}_2 \cdot \text{OH} \rightleftharpoons \text{NH}_3 : \text{O}$ . They regard the form  $\text{NH}_2\text{OH}$  as feebly acidic, since calcium displaces hydrogen from hydroxylamine, forming the compound  $\text{Ca}(\text{ONH}_2)_2$ , calcium hydroxylamate.  $\text{NH}_3 : \text{O}$  would thus be the basic form, while the hydroxylamine salts become oxonium compounds.



**Hyponitrous acid**,  $\text{H}_2\text{N}_2\text{O}_2$ , stands midway, as regards stage of oxidation, between hydroxylamine and nitrous acid. The basic properties which characterize ammonia, and are less pronounced in hydroxylamine, give place to feebly acidic properties in hyponitrous acid, which is comparable in strength

<sup>1</sup> Dunstan & Goulding, *Chem. Soc. Trans.* lxxv (1899), 1004.

<sup>2</sup> *J. pr. Chem.* 1908 [II], 78, 289.

to carbonic acid. Acidic properties are further increased in nitrous acid.

On consideration of the relationship of hyponitrous acid to hydroxylamine and to nitrous acid, the following methods of preparation may be proposed:—

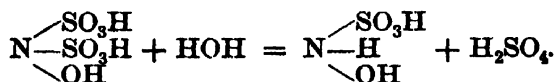
- (a) Reduction of nitrous acid.
- (b) Oxidation of hydroxylamine.
- (c) Combination of nitrous acid with hydroxylamine.

Each of these methods can be realized.

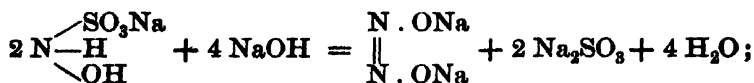
(a) Sodium hyponitrite is formed by the action of sodium amalgam on sodium nitrite solution:



Again, as was previously shown, hydroxylamine sulphonic acid is formed by the hydrolytic reduction of hydroxylamine disulphonic acid, obtained by the sulphonation of nitrous acid:



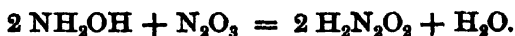
If the alkali salt of this acid is hydrolysed by fusion with caustic alkali, which does not involve reduction, hyponitrite is produced:



thus indirectly, nitrous is reduced to hyponitrous acid.

(b) Hyponitrous acid also results from the oxidation of hydroxylamine by sodium hypobromite or silver oxide.

(c) The same acid may also be prepared by introducing nitrous anhydride into a methyl alcoholic solution of hydroxylamine:



Silver hyponitrite is formed as a yellow precipitate when silver nitrate is added to a solution of the alkali salt; and thence the acid itself can be isolated by the use of ethereal hydrochloric acid. On evaporation of the ether the acid remains as a white,

crystalline solid, which dissolves in cold water; but its solution decomposes on warming, with evolution of nitrous oxide.

The molecular weight of hyponitrous acid, determined by the cryoscopic method, corresponds with the formula  $\text{H}_2\text{N}_2\text{O}_2$ . This, together with its modes of formation and acid properties, indicates that it is diazodihydroxide. It is possible, in accordance with the Hantsch-Werner view of the stereochemistry of nitrogen, that such a substance may exist in two stereoisomeric forms, known respectively as syn- and anti- forms:



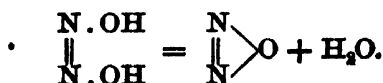
If two such bodies did exist, the syn-form should yield nitrous oxide and water more easily than the anti-form, owing to the closer proximity of the hydroxyl groups.

An isomer of hyponitrous acid exists in nitramide, the amide of nitric acid. This substance is obtained by acidic hydrolysis of salts of nitrocarbamic acid:

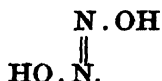


Nitramide crystallizes in white leaflets, which melt at  $72^\circ - 75^\circ$  with rapid decomposition. Its aqueous solution is strongly acid; and its salts easily decompose in solution, giving off nitrous oxide.

These facts do not accord with the idea that the substance is the amide of nitric acid. There are two views as to its constitution. Thiele believes it to be imidonitric acid,  $\text{HN}=\text{N} \begin{array}{c} \text{O} \\ \diagup \end{array} \text{OH}$ , both hydrogen atoms being replaceable by metals. Hantsch is of opinion that this substance is syndiazo-hydroxide, owing to the great ease with which it yields nitrous oxide by decomposition when heated:



Under these circumstances hyponitrous acid would be antidi-azohydroxide:



It was shown on page 193 that hyponitrous acid may be regarded as a dehydration product of **dihydroxyammonia**,  $\text{NH}(\text{OH})_2$ . This substance, also called **nitroxyl**, is formed by the oxidation of hydroxylamine by Caro's acid.<sup>1</sup>

**Nitrous acid**, the final oxidation product of ammonia, is more unstable than hyponitrous acid, for, unlike the latter substance, it cannot be obtained pure. The ortho-form,  $\text{N}(\text{OH})_3$ , is unknown, even in combination, the nitrites being meta-salts,  $\text{NO.OH}$ . These salts are very stable, but when the acid is liberated it undergoes spontaneous self-oxidation and reduction in the following manner:—



A solution of nitrous acid, obtained by dissolving its anhydride in water at low temperature, undergoes the same change on warming.

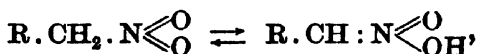
When silver nitrite reacts with an alkyl iodide a nitro-paraffin, or a mixture of nitroparaffin with alkyl nitrite, is produced. Methyl iodide gives nitromethane,  $\text{CH}_3.\text{NO}_2$ , only, ethyl iodide yields a mixture of nitroethane,  $\text{C}_2\text{H}_5.\text{NO}_2$ , and ethyl nitrite,  $\text{C}_2\text{H}_5.\text{O}.\text{NO}$ ; and the proportion of nitro-derivative diminishes with rise in the homologous series. From this it must be concluded either that silver nitrite can exist in the two forms  $\text{Ag}.\text{O}.\text{NO}$  and  $\text{Ag}.\text{NO}_2$ , or, if in the first form only, that alkyl nitrites undergo partial or complete transformation into nitroparaffins. Since the proportion between the amount of nitrite and nitro-compound formed varies when different alkyl compounds are used, it seems reasonable to assume that the phenomenon depends on the alkyl compound rather than on the structure of silver nitrite, but it is possible to assume a lability of the constituent atoms of the

<sup>1</sup> For an account of this substance see Stewart's *Recent Advances in Physical and Inorganic Chemistry*.



nitrite ion as the original cause of the production of isomers, although the extent of tautomeric change in the ion is determined by the nature of the alkyl iodide used. In the present state of knowledge, therefore, it is not possible to say whether nitrites exist in two forms or not.

A remarkable property of nitroparaffins is their acidity. This is accounted for by supposing that the following tautomeric change takes place:—

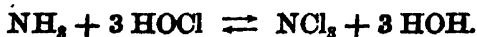


a metallic atom replacing the hydroxylic hydrogen in salt formation (*cf.* nitramide). This supposition is borne out by the fact that in certain cases<sup>1</sup> the two forms here represented have been isolated, one of them being shown to contain a hydroxyl group by giving a colour with ferric chloride.

#### NITROGEN TRIHALIDES

Nitrogen forms compounds with all the halogen elements, those with chlorine and iodine being the best known. They are endothermic compounds which are explosive, chloride of nitrogen being a very dangerous substance. These compounds are prepared by the action of the halogens, or of acids of the type HOX, on ammonia or ammonium salts.

Nitrogen trichloride is obtained as a heavy yellow oily liquid with a pungent odour by passing chlorine into a concentrated solution of ammonium chloride. If ammonia gas or solution is employed nitrogen only is obtained, together with hydrogen chloride. Nitrogen chloride is also formed when a lump of ammonium chloride is suspended in a concentrated solution of hypochlorous acid; and since  $\text{NCl}_3$  is decomposed by water into ammonia and hypochlorous acid, the following reaction is reversible:—

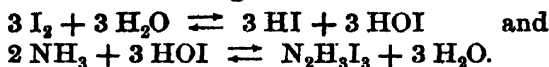


<sup>1</sup> *e.g.* Phenylnitromethane,  $\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{NO}_2$ , a pseudo acid, passing into



This reaction is of interest, since it is one of hydrolytic reduction, analogous to the acidic hydrolysis of nitrilosulphonic acid,  $N \cdot (SO_3H)_3$ , in which ammonia is generated.  $NCl_3$  can hardly therefore be considered to be the chloride of orthonitrous acid, since no nitrous acid is produced in its hydrolysis.

**Nitrogen iodide.**—By the action of iodine on aqueous ammonia the compound  $N_2H_3I_3$  is obtained as a coloured crystalline explosive substance, which is decomposed by water in the same way as chloride of nitrogen. Thus the reactions are:

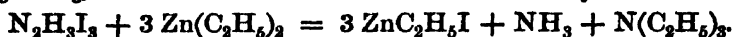


The final products of the action of water on  $N_2H_3I_3$  are ammonium iodide and iodate, formed by the self-oxidation and reduction of ammonium hypoiodite,  $NH_4OI$ .

Nitrogen iodide is best prepared, however, by adding iodine chloride to ammonia solution at  $0^\circ$ .

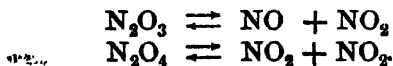


According to Silberrad<sup>1</sup> this substance has the constitution  $NH_3 : NI_3$ , since it reacts thus with zinc ethyl:



#### OXIDES OF NITROGEN, $N_2O$ , $NO$ , $N_2O_3$ , and $N_2O_4$

All these oxides can be obtained from nitric acid by the action upon it of metals or other reducing agents. The two latter can only exist in the state indicated by the above formulæ at low temperature. With rise of temperature dissociation takes place as follows:—



$N_2O$  and  $NO$ , nitrous and nitric oxides respectively, are neutral oxides; for although  $N_2O$  is formed from hyponitrous acid by loss of water, it is incapable of combining with water or bases to form this acid or its salts. Nitric oxide is essentially an unsaturated substance, for although it does not form

double molecules like  $\text{NO}_2$ , it combines with liquid nitrogen peroxide at low temperature to form  $\text{N}_2\text{O}_3$ , and with chlorine to form nitrosyl chloride.

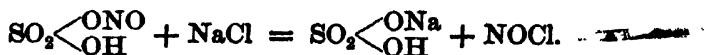
Nitric oxide can be condensed to a colourless liquid which boils at  $-153.6^\circ$  under atmospheric pressure, whilst liquid nitrous oxide boils at  $-88^\circ$ .

Nitrous and nitric oxides are both endothermic compounds, their heats of formation being  $-177 \text{ K}$  and  $-216 \text{ K}$  respectively. Like other endothermic compounds they can be detonated with fulminating mercury.

**Nitrogen trioxide**,  $\text{N}_2\text{O}_3$ , exists as an indigo-blue liquid at low temperature. When this liquid evaporates it dissociates<sup>1</sup> almost completely into  $\text{NO}$  and  $\text{NO}_2$ .  $\text{N}_2\text{O}_3$  is the anhydride of nitrous acid, and dissolves in water at  $0^\circ$  to form a blue liquid which contains the acid.

**Nitrogen tetroxide or peroxide** exists as a colourless crystalline solid ( $\text{N}_2\text{O}_4$ ) at  $-20^\circ$ . The crystals melt at  $-12^\circ$ , forming a yellow liquid, which becomes darker as the temperature rises. This liquid boils at  $26^\circ$ , giving a brown gas, which increases in intensity of colour with diminishing density on further heating, until finally it consists of molecules of  $\text{NO}_2$  only. Nitrogen peroxide is a mixed anhydride, giving rise to nitrous and nitric acids on combination with water.

**Nitrosyl chloride**,  $\text{NOCl}$ , the chloride of nitrous acid, may be prepared by heating nitrosylsulphuric acid (chamber crystals) with sodium chloride:



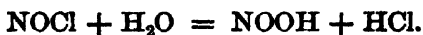
It is also formed by the direct combination of nitric oxide and chlorine. It is present in aqua regia:



Nitrosyl chloride is a reddish-yellow gas at ordinary temperature, but it can be condensed to a red liquid, which boils at

<sup>1</sup> It has been shown by Baker and Baker (*Chem. Soc. Trans.* xci (1907), 1863) that perfectly dry nitrogen trioxide evaporates without dissociation, and that the gas contains some polymerized molecules, probably of  $\text{N}_4\text{O}_6$ .

+ 2°. That it is the chloride of nitrous acid is shown by its manner of decomposition by water:

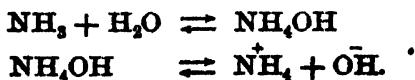


#### NX<sub>5</sub> TYPE

NH<sub>5</sub> is not known, nor is any pentahydride. The apex of the curve representing power of combination of elements with hydrogen is reached with methane, CH<sub>4</sub>. The ammonium compounds might be considered as derivatives of the NH<sub>5</sub> type, but are better classified under the **first oxidized type, NH<sub>4</sub>OH**, since they are salts derived from **ammonium hydroxide**.

Reference has been made in the general introduction to this group to the belief in the existence of NH<sub>4</sub>OH, based upon the alkalinity of a solution of ammonia in water, which furnishes evidence of the presence of hydroxyl ions in solution. The analogy between the processes and products of neutralization of solutions of ammonia and potash or soda further supports this belief.

It must not, however, be supposed that all the ammonia which dissolves in water enters at once into chemical combination with it. An aqueous solution of ammonia approximately obeys Henry's law, which states that the amount of gas dissolved by a given quantity of a liquid varies directly as the pressure exerted by that gas on the surface of the liquid. Now this law can only apply to molecules of ammonia, and not to those of ammonium hydroxide. If a solution of ammonia is in equilibrium with an atmosphere of the gas, NH<sub>3</sub> molecules enter and leave the solution at the same rate, and the NH<sub>3</sub> molecules, constant in number, in the liquid, are likewise in equilibrium with a certain amount of NH<sub>4</sub>OH which is present. Further, some of the NH<sub>4</sub>OH in the liquid undergoes electrolytic dissociation, so that the two following reactions occur side by side, both of them being subject to the law of mass:—



It has been shown that a one-per-cent solution of  $\text{NH}_3$  in water contains only about half a per cent of its ammonia in the form of dissociated  $\text{NH}_4\text{OH}$  molecules. This solution may be completely neutralized by a solution of hydrochloric acid, because the removal of  $\text{OH}$  ions from the solution by union with  $\text{H}$  ions of the acid brings about the further dissociation of  $\text{NH}_4\text{OH}$ , followed by fresh combination of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  so as to restore equilibrium. Thus, eventually, no  $\text{NH}_3$  remains in the solution, which contains only  $\text{NH}_4$  and  $\text{Cl}$  ions and a small amount of undissociated  $\text{NH}_4\text{Cl}$ .

Reference has frequently been made in previous chapters to the hydrolysis of salts in solution. Thus it has been seen that normal salts of strong acids with weak bases react acid, and that similar salts of strong bases with weak acids react alkaline in aqueous solution; aluminium sulphate and sodium carbonate serve respectively as examples. Ammonium salts undergo hydrolysis to a greater or less extent when their solutions are boiled, and since ammonia gas escapes these solutions invariably become acid. It has been shown by Veley<sup>1</sup> that the acidity produced by hydrolysis and loss of ammonia at equivalent dilution varies from an inappreciable amount with the bromide and chloride, salts of strong acids, to a moderate degree with the sulphate and chlorate; and that the largest amount of decomposition takes place with the salts of weak organic acids, such as succinic and citric acids. Thus the retention of ammonia depends directly on the strength of the acid with which it is combined, the quantitative results of hydrolysis following the order of the affinity constants of the acids.

The type  $\text{NH}_3(\text{OH})_2$  is not represented, though derivatives of the anhydrous type  $\text{NX}_3\text{O}$  are known in the oxyamines, to which reference has already been made.

No representatives of the type  $\text{NH}_2(\text{OH})_3$  are known. It may be pointed out that this degree of oxidation corresponds in phosphorus to hypophosphorous acid,  $\text{PH}_2\text{OOH}$ , which may be considered a dehydration product of hypothetical  $\text{PH}_2(\text{OH})_3$ .

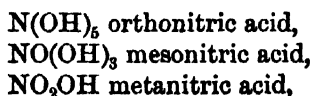
<sup>1</sup> *Chem. Soc. Trans.* lxxxvii (1906), 26.

The type  $\text{NH}(\text{OH})_4$  corresponds in its dehydrated form  $\text{NH} \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}$  to the nitro-bodies. Such substances may be considered as derived from nitric acid by reduction, since the reaction,



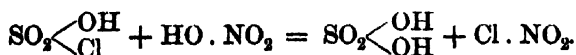
shows the conversion of the replaced hydrogen of the body undergoing nitration into a constituent of the water molecule, a process of oxidation.

Of the three types representing **nitric acid**,

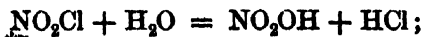


only the last is certainly known. It is true that hydrates, such as  $\text{HNO}_3$ ,  $\text{H}_2\text{O}$  and  $\text{HNO}_3 \cdot 2\text{H}_2\text{O}$ , exist, to which the first two formulæ might be attributed; but inasmuch as these compounds are unstable, and do not constitute polybasic acids, it is doubtful whether the above formulæ can correctly be applied to them.

The chloride of nitric acid,  $\text{NO}_2\text{Cl}$ , **nitroxyl** or **nitryl chloride**, is said to be formed by the direct union of nitrogen peroxide and chlorine, and also by the action of chlorosulphonic acid or of phosphorus pentachloride on nitric acid:

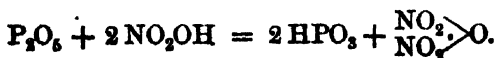


~~It has been~~ described as a yellow liquid, boiling at  $+5^\circ$ , being decomposed by water after the manner of all acid chlorides, thus:

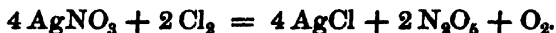


but its existence is doubtful.

The last dehydration product of orthonitric acid, **nitric anhydride**, is obtained as a white, deliquescent crystalline substance by distilling anhydrous nitric acid with phosphoric oxide:



It was originally prepared, however, by passing dry chlorine over dry silver nitrate, gently heated:



## PHOSPHORUS

The molecules of nitrogen and phosphorus differ widely from one another. The molecules of nitrogen are diatomic; for, whilst the constituent atoms are firmly united together, so that the molecule resists disruption and is chemically inert, no tendency is shown towards further condensation, since no allotropic forms of nitrogen exist; and the element passes into the liquid state at very low temperature only.

The molecules of phosphorus vapour are tetratomic for temperatures considerably above the boiling-point of the element; only when the vapour is heated very strongly does dissociation into diatomic molecules take place. Phosphorus, too, is easily condensed, its boiling-point and melting-point under atmospheric pressure being  $287^\circ$  and  $44^\circ$  respectively, whilst those of nitrogen are  $-194^\circ$  and  $-214^\circ$ . Phosphorus, further, shows a tendency to polymerize, with production of an allotropic form.

**Ordinary, or waxy phosphorus,  $P_4$ ,** crystallizes from solvents, such as carbon disulphide, and by sublimation *in vacuo*, in forms belonging to the regular system.

**Red phosphorus,  $P_8$ ,** often called amorphous phosphorus, is obtained by heating  $P_4$  to  $250^\circ$ , out of contact with air. This transformation also goes on slowly at atmospheric temperature when  $P_4$  is exposed to light, and is promoted by certain catalytic agents, such as a crystal of iodine;  $P_8$  crystallizes in rhombohedra, belonging to the hexagonal system, though in the form of red phosphorus the crystals are ill-defined. This form is insoluble in carbon disulphide, and is in various ways less active than  $P_4$ . The conversion of  $P_4$  into  $P_8$  is an exothermic reaction,  $P_8$  being the more stable

form.  $P_2$  may be obtained from  $P_8$  by subliming and condensing the vapour; this is in accordance with the principle that the less stable form appears first under such circumstances.

**Scarlet phosphorus.**—A bright red form of phosphorus, known as Schenck's scarlet phosphorus, is produced when ordinary phosphorus is boiled with its tribromide. It is amorphous and chemically active, but not poisonous, and is now being substituted for ordinary phosphorus in the manufacture of matches.

#### HYDRIDES OF PHOSPHORUS

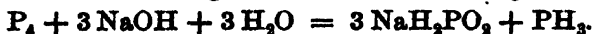
Four hydrides of phosphorus, or phosphides of hydrogen, appear to be known:

$PH_3$	Phosphine, or gaseous hydrogen phosphide.
$P_2H_4$	liquid                   "                   "
$P_{12}H_6$	solid                   "                   "
$P_9H_2$	

$PH_3$  is the analogue of ammonia, and  $P_2H_4$  that of hydrazine, but no nitrogen analogue of  $P_{12}H_6$  or  $P_9H_2$  is known.

**Phosphine**, like ammonia, can be obtained by the hydrolysis of its halide salts. Alkalis or water may be used; but whereas ammonium chloride yields very little ammonia when boiled with water, phosphonium iodide is easily and completely hydrolysed by cold water. This difference is due to the slightly basic character of phosphine as compared with ammonia, and the accompanying slight stability of its salts.

Phosphine is usually prepared, however, by heating ordinary phosphorus with caustic alkali solution. The following is the reaction, for which nitrogen furnishes no analogue:—



This, however, does not represent all that happens, for a certain amount of  $P_2H_4$  is produced which renders the  $PH_3$  spontaneously inflammable.

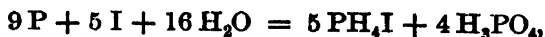
Phosphine is produced by the action of dilute acid on metallic phosphides (cf.  $H_2S$ ), and also by heating hypophosphorous and phosphorous acids and their salts.

<sup>1</sup> Stock, Böttcher, and Lenger, Ber, 1900, 42, 2247.



Phosphine is a powerful reducing agent, precipitating mixtures of metal and phosphide from solutions of cupric and silver salts. It is more readily decomposed by electric sparks than ammonia, and much more inflammable than this gas, its temperature of ignition being so low that it may sometimes be ignited by the heat of friction caused by removal of the stopper from a bottle containing it. The final products of its combustion are phosphoric oxide and water.

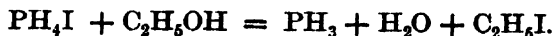
The fact that it is only slightly soluble in water, and that its solution is not alkaline, shows that its basic properties are of the feeblest possible description. It will, however, unite directly with hydrogen halides to form salts, the best known of which is phosphonium iodide. This compound, prepared by the action of water on an intimate mixture of phosphorus and iodine:



crystallizes in colourless quadratic prisms which may be sublimed. It fumes in moist air owing to hydrolytic decomposition. Ammonia displaces phosphine:



and alcohol decomposes the compound as follows:—

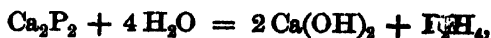


It is used as a reducing agent, and for the preparation of organic phosphines, for instance:—

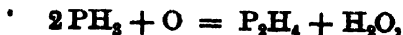


Phosphonium bromide and chloride are even more unstable than the iodide. They are obtained by combination of phosphine with the hydrogen halides under pressure.

$P_2H_4$ , or liquid hydrogen phosphide, may be obtained by the action of water on calcium phosphide,  $Ca_2P_2$ :



and results also from the oxidation of phosphine:



which may be effected by means of nitric oxide. It is condensed by passage through a cooled tube to a colourless liquid which boils at about  $60^\circ$ ; this liquid is very unstable, and easily decomposes in sunlight into  $\text{PH}_3$  and  $\text{P}_{12}\text{H}_6$ :



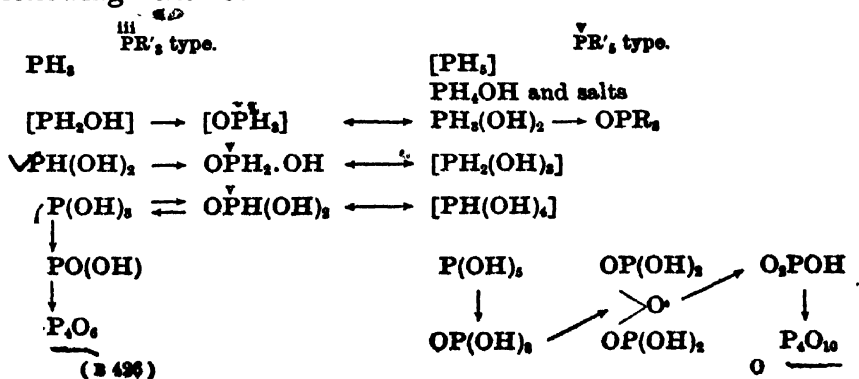
The decomposition is promoted by hydrochloric acid, so that phosphine may be freed from the liquid hydride and deprived of its spontaneous inflammability, by bubbling through hydrochloric acid.

This hydride is not known to form any organic derivatives of the type  $\text{H}_2\text{P} \cdot \text{PHR}$  analogous to phenylhydrazine,  $\text{H}_2\text{N} \cdot \text{NHC}_6\text{H}_5$ . The hydride,  $\text{HP}=\text{PH}$ , does not exist, but a consideration of the grouping  $-\text{P}=\text{P}-$  recalls the diazo grouping  $-\text{N}=\text{N}-$  and the series of compounds derived therefrom. Diphospho derivatives have been obtained; for instance,  $\text{C}_6\text{H}_5\text{P}:\text{PC}_6\text{H}_5$ , as well as  $\text{C}_6\text{H}_5\text{P}:\text{POH}$ . This latter compound differs, however, from diazobenzene in its manner of preparation and the fact that it is not basic.

Triphospho derivatives,  $\text{MP} \begin{smallmatrix} \nearrow \text{P} \\ \parallel \\ \searrow \text{P} \end{smallmatrix}$ , corresponding to azoimide and its salts,  $\text{MN} \begin{smallmatrix} \nearrow \text{N} \\ \parallel \\ \searrow \text{N} \end{smallmatrix}$ , are not known.

#### OXYGEN DERIVATIVES OF PHOSPHORUS

The oxygen derivatives of phosphorus are shown in the following scheme:—

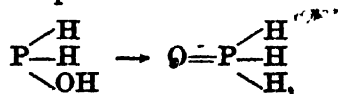


In addition to the above, a suboxide,  $P_4O$ , is said to exist; there is also an oxide,  $(PO_2)_n$ , together with an acid,  $H_2PO_3$ , corresponding to the same degree of oxidation.

**Phosphorus suboxide**,  $P_4O$ , is said to be formed when finely divided yellow phosphorus is digested with one volume of 10-per-cent caustic-soda solution, and two volumes of alcohol. The solution becomes dark red, and phosphine and hydrogen are slowly evolved. When the solution is acidified with hydrochloric acid the supposed suboxide is obtained as a dark-yellow or reddish powder. It has been shown, however, by Chapman, Lidbury, and Burgess<sup>1</sup> that this powder always contains more phosphorus than corresponds to the formula  $P_4O$ ; and that it probably consists of impure red phosphorus containing oxygen, hydrogen, and other impurities, since it is very hygroscopic, and undergoes local oxidation by reason of the water it retains. Corresponding to the unknown oxide  $PO$  and the liquid hydride  $P_2H_4$  is the iodide  $P_2I_4$ , obtained by bringing the elements together in theoretical proportions in carbon disulphide solution, and evaporating. This iodide is a yellow, crystalline mass, melting at  $110^\circ$ , and giving a vapour density corresponding to the above formula.

#### TRIVALENT PHOSPHORUS DERIVATIVES

Considering the type  $PR'_3$ , the first oxidation product of  $PH_3$  should be  $PH_2OH$ , corresponding to hydroxylamine,  $NH_2OH$ . This substance is not known, and it seems probable that it could not exist, or at least that it would be very unstable, for all hydroxylated derivatives of trivalent phosphorus show a tendency to undergo tautomeric change in such a manner as to become pentavalent. Thus the change

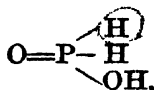


were the compound known, would be consistent with the behaviour of known compounds, which are referred to below, the phosphorus atom assuming pentavalency wherever possible

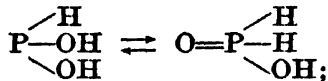
<sup>1</sup> *Chem. Soc. Trans.*, lxxv, 973, and lxxix, 1235.

in its oxygen compounds in accordance with its oxidizability. Indeed the type  $\text{OP} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix}$  represents the most stable and characteristic grouping of the phosphorus atom. Numerous alkylated oxyphosphines, for instance  $\text{OP}(\text{CH}_3)_3$ , have been prepared by A. Michaelis.

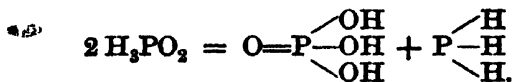
The formula  $\text{PH}(\text{OH})_2$  corresponds to the stage of oxidation of hypophosphorous acid. Now this acid is strictly monobasic, and such a property does not accord well with the above formula, since the hydroxylic hydrogen will be replaced by metals in preference to the hydrogen attached directly to phosphorus. This makes it probable that the constitution of hypophosphorous acid is rather



or that possibly one of the hydrogen atoms is in a labile condition, thus:—



so that inorganic salts, at least of the dibasic form, cannot permanently exist. This tendency of phosphorus to pass over into the form  $\text{OP} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix}$  is well brought out by the effect of heat on hypophosphorous acid and its salts, when phosphoric acid and phosphine are produced; thus:—



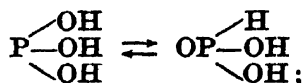
It will be observed that whilst hypophosphorous and hyponitrous acids may be conceived as derived from the same type of oxidation,  $\text{R}'''\text{H}(\text{OH})_2$ , similarity between their constitution ends here.

† **Hypophosphorous acid**,  $\text{H}_3\text{PO}_2$ , may be obtained in a crystalline form by decomposing its barium salt with dilute sulphuric acid and evaporating the solution. It melts at  $17^\circ$ , and on

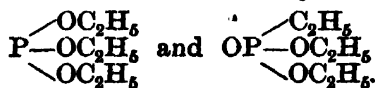
being heated undergoes the above change. It is a powerful reducing agent, precipitating gold, silver, and mercury from their salts. It is distinguished from phosphorous acid, which behaves in a similar manner, by the solubility of its barium salt, and by precipitating cuprous hydride,  $\text{Cu}_2\text{H}_2$ , as a red powder, when warmed with copper-sulphate solution and acetic acid.

Neither the anhydride nor the chloride of hypophosphorous acid is known.

The type  $\text{P}(\text{OH})_3$  represents symmetrical phosphorous acid. As regards the existence of a substance of this constitution, the following remarks may be made. Phosphorous acid is always dibasic in its solid inorganic salts, although  $\text{Na}_3\text{PO}_3$  is supposed to exist in solution, and the ester  $\text{P}(\text{OC}_2\text{H}_5)_3$  is known. Ostwald explains the dibasicity of this acid by assuming that ionisation only proceeds as far as  $2\text{H}$  and  $\text{HPO}_3$ , since it is well known that polybasic acids are completely ionised with difficulty. Phosphoric acid, for instance, is ionised into  $\text{H}$  and  $\text{H}_2\text{PO}_4$ ; but phosphoric acid is tribasic. Arsenious acid is even tribasic, since  $\text{Ag}_3\text{AsO}_3$  is known, although it is probably a weaker acid than phosphorous acid. It would appear, therefore, that the reason for the dibasicity of this acid in its inorganic salts must be sought in another direction. All the facts are satisfactorily explained by supposing that phosphorous acid undergoes the following tautomeric change:—



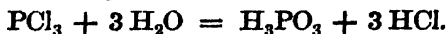
so that its dibasicity depends on the tendency for self-oxidation manifested by phosphorus compounds. Corresponding to these two formulæ are the isomeric ethyl esters:



Phosphorous acid when heated breaks up in a similar way to hypophosphorous acid, thus:



✕ **Phosphorous acid**,  $\text{H}_2\text{PO}_3$ , is formed by the slow oxidation of phosphorus in moist air, or by the decomposition of the chloride of the acid by cold water:



After removal of water and hydrochloric acid by evaporation the phosphorous acid crystallizes as a deliquescent mass which melts at  $70^\circ$ . A solution of the acid or its salts reduces salts of gold, silver, and mercury, and precipitates sulphur from sulphurous acid.

✕ **Phosphorous anhydride**,  $\text{P}_4\text{O}_6$ , is produced, together with phosphoric anhydride, by the slow combustion of phosphorus in a tube through which air is drawn. It may be obtained in crystals which melt at  $22.5^\circ$ , and boil at  $173^\circ$  in an indifferent atmosphere. It forms phosphorous acid by combination with cold water, but hot water decomposes it, producing red phosphorus, hydrogen phosphide, and phosphoric acid. When heated gently it burns to phosphoric oxide, but when quickly heated to  $440^\circ$ , it decomposes into red phosphorus and phosphorus tetroxide. Determination of vapour density leads to the formula  $\text{P}_4\text{O}_6$ .

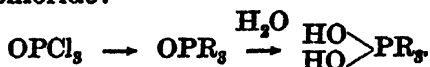
The **chloride of phosphorous acid**, **phosphorus trichloride**,  $\text{PCl}_3$ , is formed when phosphorus burns in chlorine, or when a current of dry chlorine is led over phosphorus. It is a colourless liquid, boiling at  $76^\circ$ . Cold water decomposes it, forming hydrochloric and phosphorous acids. Hot water gives phosphoric acid and lower oxides of phosphorus. It is susceptible of easy oxidation to phosphoryl chloride,  $\text{POCl}_3$ .

#### PENTAVALENT PHOSPHORUS DERIVATIVES

Passing to the derivatives of pentavalent phosphorus, it will suffice to point out that of the hypothetical types,  $\text{PH}_3(\text{OH})_2$ ,  $\text{PH}_2(\text{OH})_3$ ,  $\text{PH}(\text{OH})_4$ , the first represents a hydroxylated form corresponding to the oxyamines previously considered, and that the latter two correspond respectively to hydroxylated forms of hypophosphorous and unsymmetrical phosphorous acids.

With regard to the orthophosphoric type,  $\text{P}(\text{OH})_5$ , although no salts of a pentavalent phosphoric acid are known, Michaelis

has obtained corresponding organic hydroxylated derivatives of phosphoryl chloride:



Whilst  $\text{P}(\text{OH})_3$  and its salts do not appear to exist, the first dehydration product,  $\text{PO}(\text{OH})_2$ , is stable at ordinary temperature, both in the solid state and in solution. It is therefore known as orthophosphoric acid.

Further dehydration may involve either a single molecule, thus:—

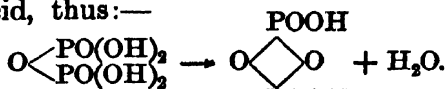


or two, thus:—

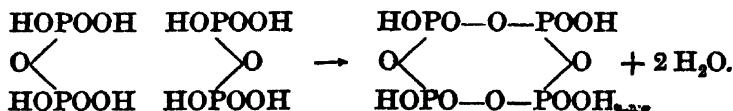


the product in the first case being metaphosphoric, and in the second, pyrophosphoric acid.

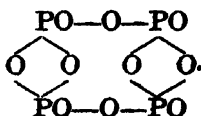
If a molecule of pyrophosphoric acid lost a molecule of water in the same sense as the original ortho-acid lost a molecule to form the pyro-acid, there would result dimetaphosphoric acid, thus:—



If two molecules were involved in this condensation instead of only one, there would result tetrametaphosphoric acid, thus:—

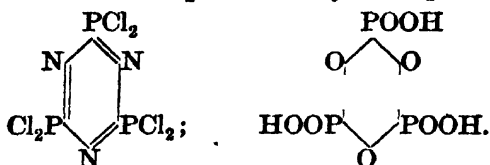


These polymerised phosphoric acids are known,<sup>1</sup> and it is now only a step, from the point of view of constitution, from tetrametaphosphoric acid to phosphoric anhydride,  $\text{P}_4\text{O}_{10}$ , which may be represented thus:—



<sup>1</sup> Parravano and Calcagni (*Atti R. Accad. Lincei*, 1908 [v], 17, 1, 731) maintain, however, that these polyphosphates are but mixtures of meta- and pyrophosphate.

The above instances do not, however, exhaust the tendency to polymerisation exhibited by this class of compounds. Instances of polymerisation into threefold union are known among carbon compounds; for example, the conversion of aldehyde into paraldehyde and acetylene into benzene. Some phosphoric compounds display a like tendency. The compound  $\text{NPCl}_2$ , for instance, when formed from  $\text{PCl}_5$  and  $\text{NH}_3$  at a temperature of  $175\text{--}200^\circ$ , consists of molecules  $(\text{NPCl}_2)_3$  which may be compared with trimetaphosphoric acid  $(\text{HPO}_3)_3$ . The constitution of these two compounds may be represented thus:—

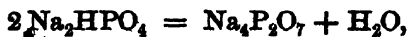


Hexametaphosphoric acid,  $\text{H}_6\text{P}_6\text{O}_{18}$ , probably contains a twelve-membered ring.

**Phosphoric anhydride**, or phosphoric oxide,  $\text{P}_4\text{O}_{10}$ , the product of the complete combustion of phosphorus in air or oxygen, is a white, amorphous, hygroscopic solid, which when heated yields a crystalline sublimate. It is a powerful dehydrating agent, combining with water to form metaphosphoric acid.

**Orthophosphoric acid**,  $\text{H}_3\text{PO}_4$ , obtained as a crystalline mass by evaporating its solution, melts at  $38^\circ$ . When heated to  $213^\circ$  it loses water, forming the pyro-acid, together with some meta-acid. Stronger heating produces the meta-acid.

The sodium salt of pyrophosphoric acid is formed by the ignition of ordinary sodium phosphate,



whence a solution of the acid may be obtained by precipitating the lead salt and then decomposing it with hydrogen sulphide.

Sodium metaphosphate is obtained by igniting either sodium dihydrogen phosphate, or microcosmic salt:





and metaphosphoric acid itself by heating ordinary ammonium phosphate,



as well as by the ignition of phosphoric acid, and by the deliquescence of phosphoric oxide in moist air.

†Pyrophosphoric acid is obtained as a vitreous mass by evaporating its solution in a vacuum. The meta-acid is also vitreous, and is commonly known as glacial phosphoric acid. It does not form the anhydride when heated, but volatilizes unchanged.

When either meta- or pyro-phosphoric acid remains in contact with water, and especially on heating, hydration proceeds as far as the tribasic acid,  $\text{H}_3\text{PO}_4$ , which is therefore the most stable form at ordinary temperatures.

Salts of the various polymeric metaphosphoric acids are formed when certain orthophosphates are ignited at suitable temperatures.

#### CHLORIDES OF PHOSPHORIC ACID

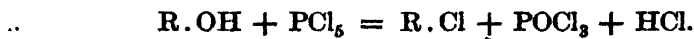
Phosphorus pentachloride, or phosphoric chloride,  $\text{PCl}_5$ , corresponds to the hypothetical ortho-acid,  $\text{P}(\text{OH})_5$ , and phosphoryl chloride, or phosphorus oxychloride,  $\text{POCl}_3$ , to ordinary phosphoric acid; whilst  $\text{P}_2\text{O}_5\text{Cl}_4$  is the chloride of pyrophosphoric acid. The chloride of metaphosphoric acid is unknown. Phosphorus pentachloride is prepared by the action of chlorine on the trichloride. It is a pale-yellow crystalline solid which fumes in moist air.

Whilst neither phosphoric oxide nor its hydration products lose oxygen when heated, phosphoric chloride dissociates into phosphorus chloride and chlorine at a moderate temperature.

The superior stability of the oxide molecule is probably due to spatial relationships and to the greater power of persistence of the type  $\text{OP} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix}$ , as compared with  $\text{Cl}_2\text{P} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix}$ . It may be observed that phosphoryl chloride,  $\text{OP} \begin{smallmatrix} \diagup \text{Cl} \\ \diagdown \text{Cl} \end{smallmatrix}$ , is not dissociated

by heat, and also that the chlorine type of compound is more comparable with the hydrogen than the oxygen type, and that no pentahydride of phosphorus is known.

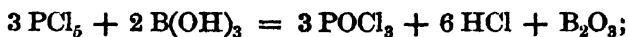
Phosphorus pentachloride is employed, especially in organic chemistry, for the substitution of Cl for OH, according to the following general reaction:—



\* **Phosphoryl chloride**, or **phosphorus oxychloride**,  $POCl_3$ , is the first product of the action of water on  $PCl_5$ :



It may be prepared according to this principle by the use of boric acid, thus:—



also by the action of phosphoric oxide upon the chloride:

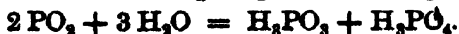


and by the direct oxidation of  $PCl_3$ . It is a colourless, mobile liquid, distilling unchanged at  $107^\circ$ . It is decomposed by water into meta- or orthophosphoric acid.

**Pyrophosphoryl chloride**,  $P_2O_3Cl_4$ , is a colourless, fuming liquid, boiling at  $210$ – $215^\circ$ ; and thereby suffering partial decomposition into  $POCl_3$  and  $P_4O_{10}$ . It is obtained, together with other products, by the oxidation at low temperature of phosphorus trichloride by nitrogen peroxide.

**Phosphorosophosphoric oxide**,  $(PO_2)_n$ , and **hypophosphoric acid**,  $H_2P_2O_6$ , remain to be considered.

Phosphorosophosphoric oxide is obtained by the partial combustion of phosphorus; and also from phosphorous oxide, which, when heated to  $440^\circ$  decomposes into red phosphorus and  $(PO_2)_n$ . This latter compound forms colourless crystals which do not melt at  $100^\circ$ ; its vapour density at about  $1400^\circ$  is 230, which corresponds nearly to the molecular formula  $P_8O_{16}$ . Its solution in cold or boiling water reduces mercuric and silver salts, and contains phosphorous and phosphoric acids:



Phosphorosulphosphoric oxide is therefore a mixed anhydride, and is in this respect analogous to nitrogen tetroxide, which dissolves in water to form nitrous and nitric acids.

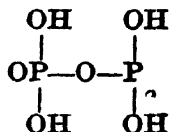
**Hypophosphoric acid**, which has the empirical formula  $\text{H}_2\text{PO}_3$ , is obtained by the slow oxidation of phosphorus in moist air, and may be separated from the other acids produced at the same time by forming the sparingly soluble sodium salt,  $\text{NaHPO}_3 \cdot 3\text{H}_2\text{O}$ . The acid itself may be obtained in crystals containing one molecule of water,  $\text{H}_2\text{PO}_3 \cdot \text{H}_2\text{O}$ , and melting at  $62^\circ$ , by decomposing the barium salt with dilute sulphuric acid, and evaporating the filtered solution under reduced pressure. The molecular formula of hypophosphoric acid has been a matter of controversy. It was originally thought to be  $\text{H}_4\text{P}_2\text{O}_6$ , the sodium salt by means of which it is isolated being  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ .

Parravano and Marini<sup>1</sup> conclude from variations of the electric conductivity at varying dilutions that the two sodium salts are correctly represented by the formulæ  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6$  and  $\text{Na}_4\text{P}_2\text{O}_6$ , rather than by  $\text{NaHPO}_3$  and  $\text{Na}_2\text{PO}_3$ .

On the other hand, Rosenheim, Stadler, and Jacobsohn<sup>2</sup> believe, also as the result of electric conductivity experiments, that the simpler formulæ are correct. And further, Rosenheim and Pritze<sup>3</sup> have shown that the molecular weights of the methyl and ethyl esters of hypophosphoric acid, determined by the ebulliscope method, are in accordance with the formula  $\text{H}_2\text{PO}_3$  for the acid. Nevertheless Cornec<sup>4</sup> considers the question still unsettled.

Meanwhile the constitution of the acid can be considered tentatively.

The constitution



has been attributed to hypophosphoric acid, in which this

<sup>1</sup> *Atti R. Accad. Lincei* [v], 15, 11, 208.

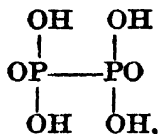
<sup>2</sup> *Ber.* (1906), 39, 2857.

<sup>3</sup> *Ber.* (1906), 41, 2708.

<sup>4</sup> *Bull. Soc. Chim.*, 1909 [1v], 5, 1081, 1121.

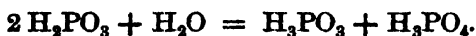
compound appears to be a mixed anhydride of phosphorous and phosphoric acids. If the acid possessed this constitution, its reducing properties would probably resemble those of phosphorous acid. It is distinguished, however, from the latter acid by the readiness with which it reduces acidified permanganate solution, and by this means it may be estimated.

-If, therefore, the molecular formula of hypophosphoric acid is  $H_4P_2O_6$ , its constitution is best represented by the formula



which shows analogy with oxalic and dithionic acids; if, however,  $H_2PO_3$  is the molecular formula, the constitution  $OP(OH)_2$ , in which phosphorus is tetravalent, is probable.

When heated with mineral acid, hypophosphoric acid is converted into a mixture of phosphorous and phosphoric acids, thus:—



#### THE SULPHIDES OF PHOSPHORUS

Several compounds of phosphorus and sulphur have been prepared by heating the elements together. The most important of these is the **pentasulphide**,  $P_2S_5$ , consisting of yellow crystals, which melt at  $274-276^\circ$  and distil unchanged. It is the thioanhydride of thiophosphoric acid, and unites with alkali sulphides to form thiophosphates,  $SP(SM')_3$ ; the chloride, **thiophosphoryl chloride**,  $SPCl_3$ , is prepared by the action upon it of phosphorus pentachloride, thus:—



The product is a colourless liquid, boiling at  $125^\circ$ .

#### ARSENIC, ANTIMONY, AND BISMUTH

These three elements present a transition from non-metallic to metallic characters, since in arsenic non-metallic properties predominate, and in bismuth, metallic properties. Arsenic is closely allied to phosphorus in the properties of the element,

and the types of compounds which it forms, and antimony similarly approximates to arsenic. Bismuth, however, shows a marked difference from the other two elements in the non-existence of a hydride and the much more pronounced basic character of its oxides. This is in accordance with the fact that a blank space occurs in the periodic classification between antimony and bismuth.

Some physical constants are here given:

	Density.	M.P.	B.P.
Arsenic ...	As <sub>α</sub> 3·88, As <sub>β</sub> 4·71, As <sub>γ</sub> 5·73	500° under increased pressure	—
Antimony ...	Sb <sub>α</sub> —, Sb <sub>β</sub> 5·3, Sb <sub>γ</sub> about 6·8	630·5°	Bright red heat
Bismuth ...	9·75	264°	Above 1090°

The melting-point of arsenic under increased pressure is lower than that of antimony, and the former element is considerably more volatile than the latter, since it begins to sublime below 100°. Arsenic exists in three allotropic modifications, which may be designated, in the reverse order of their stability, as As<sub>α</sub>, As<sub>β</sub>, As<sub>γ</sub>. This allotropy is distinctly a non-metallic characteristic, and indeed in the nature of its allotropic forms arsenic closely recalls phosphorus.

As<sub>α</sub> is produced by subliming ordinary arsenic in a stream of CO<sub>2</sub> and quickly cooling the vapour; it is a sulphur-yellow powder, which is soluble in carbon disulphide, and is probably crystalline. It recalls ordinary or waxy phosphorus. When it is heated it passes quickly into As<sub>β</sub>, or mirror arsenic, which is generally described as amorphous, but is probably crystalline. Finally, both of these varieties pass, on strong heating, into ordinary crystalline or "metallic" arsenic, As<sub>γ</sub>, which is analogous to "metallic" phosphorus.

Antimony and bismuth present a more unmistakably metallic appearance in the free state than arsenic, but antimony resembles arsenic in its allotropic forms. Sb<sub>α</sub> is yellow like As<sub>α</sub>, and is formed by oxidising stibine below - 90°; Sb<sub>β</sub>, similarly produced at - 40°, is an amorphous black powder, which passes on heating into the stable, greyish-white metallic form. In

accordance with its more metallic nature, bismuth does not exhibit allotropy.

As regards the molecular condition of their vapours, these elements show a gradation of properties. Arsenic vapour, like phosphorus, is tetratomic at moderately low temperatures, but above  $1600^{\circ}$  dissociates into diatomic molecules. The density of antimony vapour at about  $1600^{\circ}$  shows that it is a mixture of diatomic and monatomic molecules. The vapour density of bismuth between  $1600^{\circ}$  and  $1700^{\circ}$  reveals a similar molecular state. Simple molecular constitution in the state of vapour is a criterion of the metallic state; the vapours of metals being, as far as is known, for the most part monatomic. This might be assigned to the high temperature required to vaporize them, but cryoscopic measurements also show monatomicity.

The behaviour of the elements towards acids is important. Hydrochloric acid has little or no action on arsenic, antimony, or bismuth in absence of air; in presence of air the chlorides are formed. Nitric acid oxidizes arsenic to arsenic acid,  $H_3AsO_4$ , and antimony to hydrated antimonious or antimonie oxide according to the strength of the acid; this metal therefore behaves like tin towards nitric acid. Dilute nitric acid dissolves finely-divided antimony, however; probably an ill-defined nitrate is thus formed. When nitric acid acts upon bismuth the nitrate is formed in solution. Three degrees of metallic nature are here illustrated by the action of nitric acid:

- (i) formation of soluble oxyacid,
- (ii) „ „ insoluble hydrated oxide,
- (iii) „ „ soluble nitrate.

All three elements dissolve in hot concentrated, though not in dilute, sulphuric acid, with evolution of sulphur dioxide, and formation of sulphate, probably, in each case. Antimonious and bismuthous sulphates are well known. Arsenious sulphate,  $As_2(SO_4)_3$ , probably exists.

#### HYDRIDES OF ARSENIC AND ANTIMONY

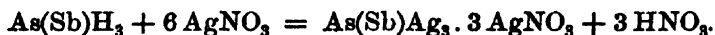
The hydrides of this group have been discussed in the Intro-

duction (p. 185); the properties of the simple hydrides of arsenic and antimony are further illustrated by the following facts:—

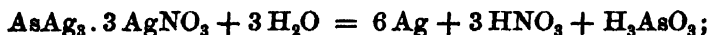
**Arsine** boils at  $-55^{\circ}$  and solidifies at  $-119^{\circ}$ .

**Stibine** „ „  $-17^{\circ}$  „ „ „  $-88^{\circ}$ .

Both these hydrides are produced by the action of nascent hydrogen upon compounds in solution, as in the familiar Marsh's test. Stibine, however, is not produced by the hydrogen generated from the action of potash solution upon zinc. Thus arsenic is distinguished from antimony in Fleitmann's test. A further distinction between the two hydrides depends upon their behaviour towards silver nitrate. With solid silver nitrate arsine and stibine produce similar yellow compounds of silver arsenide or antimonide and nitrate (Gutzeit's test), thus:



The arsenic compound is decomposed by water, thus:



but the antimony compound yields  $\text{SbAg}_3$  and  $\text{AgNO}_3$  without reduction.

If arsine is passed through a dilute solution of silver nitrate, metallic silver is at once precipitated (Hofmann's test), whilst the arsenic goes into solution as arsenious acid, thus:



In the case of stibine, however, silver antimonide is precipitated, together with some metallic silver resulting from the action of hydrogen on silver nitrate. This test serves to distinguish and separate arsenic from antimony.

The difference in behaviour in the two cases evidently depends on the superior oxidizability of arsine, which passes into solution as arsenious acid. In this respect the hydride of arsenic approximates to that of phosphorus, which is a very powerful reducing agent. That arsenic itself is more easily oxidized than antimony is shown by the solubility in hypo-

chlorite solution of the deposit obtained in Marsh's test, the corresponding antimony deposit being insoluble.

No other hydride of antimony but  $\text{SbH}_3$  is known; arsenic, however, forms the compound  $\text{As}_2\text{H}_2$ , which is a silky solid, produced by the action of water on sodium arsenide,  $\text{AsNa}_3$ . Its phosphorus analogue,  $\text{P}_2\text{H}_2$ , is not known, and the existence of  $\text{N}_2\text{H}_2$  is doubtful.

The type of hydrazine,  $\text{N}_2\text{H}_4$ , and liquid hydrogen phosphide,  $\text{P}_2\text{H}_4$ , is represented by **cacodyl**,  $\text{As}_2(\text{CH}_3)_4$ .

#### OXYGEN COMPOUNDS OF AS, Sb, AND Bi

The oxides of the types  $\text{X}_2\text{O}_3$  and  $\text{X}_2\text{O}_5$  are representative of the two main classes of compounds which these elements form. Some lower, and intermediate oxides are, however, known.

✕ **A suboxide of arsenic**,  $\text{As}_2\text{O}$ , probably exists, and is said to be formed, together with the various allotropic forms of the element, when arsenic is sublimed in an open tube.

Corresponding to the unknown oxide,  $\text{AsO}$ , is the iodide,  $\text{AsI}_2$ , formed when  $\text{AsI}_3$  is heated with arsenic in a sealed tube in presence of carbon disulphide. This compound recalls the iodide of phosphorus,  $\text{P}_2\text{I}_4$ .

The existence of a suboxide of antimony is very doubtful.

✕ **Bismuth** is said to form a **suboxide**,  $\text{BiO}$  or  $\text{Bi}_2\text{O}_2$ , which is obtained as a black precipitate by the reduction of a bismuth salt by an alkaline stannous solution. This precipitate contains metallic bismuth, and may be a mixture of the finely-divided metal and hydrated sesquioxide. **Bismuth dihalides**,  $\text{BiX}_2$ , are, however, known.

A sulphur analogue of the  $\text{R}_2\text{O}_2$  type exists in the case of arsenic. It is the disulphide,  $\text{As}_2\text{S}_2$ , which occurs naturally as **realgar**. Antimony and bismuth both form oxides,  $\text{X}_2\text{O}_4$ .

#### OXIDES OF THE TYPE $\text{X}_2\text{O}_3$ AND THEIR DERIVATIVES

✕ **Arsenious oxide**,  $\text{As}_2\text{O}_3$ , is analogous to phosphorous oxide on account of its molecular constitution, and the fact that it is an acidic anhydride. It also resembles phosphorous oxide in existing in more than one form. The vitreous form, which is transparent, is produced when ordinary "white arsenic" is

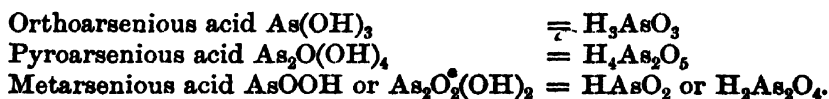


heated to its temperature of sublimation. It passes into the octahedral form when kept at ordinary temperature. It is more soluble in water than the crystalline form, but a saturated solution gradually deposits octahedral crystals. Arsenious oxide also occurs in monoclinic crystals which are isomorphous with a natural form of antimonious oxide.

The resemblance between phosphorous and arsenious oxides is slight; for whilst phosphorous oxide is unstable towards heat, arsenious oxide is quite stable, and sublimes unchanged; and whilst phosphorous oxide is easily soluble in water, arsenious oxide is very slightly soluble. The power of combining with water possessed by arsenious oxide is so slight that the acid itself has never been obtained, evaporation of its solution causing the separation of the oxide.

Arsenious oxide dissolves in sodium hydroxide and carbonate solutions, forming arsenites, though from hot concentrated solutions the oxide again separates on cooling; it also dissolves in hydrochloric acid, owing to the formation of arsenious chloride, though from a concentrated solution arsenious oxide gradually separates in well-formed crystals. The presence of the volatile arsenious chloride in such a solution is proved by its appearance in the liquid obtained by distillation.

**Arsenious acid.**—Arsenious oxide is slightly soluble in water, forming a solution with a feebly acid reaction. This solution contains orthoarsenious acid, *i.e.* arsenious oxide in a state of complete hydration. Salts corresponding to ortho-, pyro-, and meta-arsenious acid are known; to these acids the following formulæ may be attributed:—

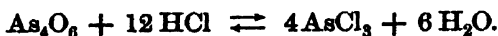


Salts of pyro- and meta-, as well as of orthoarsenious acid, are obtained by precipitation or crystallization from solution, not by ignition. The alkali arsenites, which are soluble in water, are metasalts; most pyro and ortho arsenites are insoluble.

All arsenites are easily decomposed, since arsenious acid is very weak; carbonic acid or hydrogen sulphide suffices for this purpose. The soluble arsenites react alkaline, owing to hydrolytic dissociation. There is no reason to regard arsenic as other than trivalent in arsenious compounds, arsenic thus differing from phosphorus in analogous compounds.

Arsenious acid is a reducing agent, precipitating cuprous oxide from an alkaline cupric solution. It does not, however, possess such powerful reducing properties as phosphorous acid. Its reaction with iodine is well known. Arsenic in the condition of arsenious compounds may be reduced to the state of the element when in solution, as well as when heated in the solid state with reducing agents. For instance, a solution of stannous chloride produces As and  $\text{AsH}_3$ .

**Arsenious chloride**,  $\text{AsCl}_3$ , the chloride of arsenious acid, may be obtained by the action of chlorine on the element, or of hydrochloric acid on arsenious oxide. The latter method of formation suggests that this compound is a salt. And indeed by some of its properties it is thus characterized. It is a colourless liquid, boiling at  $130^\circ$ , and soluble in organic solvents, like other chloranhydrides. It does not immediately give arsenious oxide with water, but first forms the crystalline compound  $\text{AsCl}(\text{OH})_2$ , which may be considered a basic salt. Eventually  $\text{As}_4\text{O}_6$  separates, and so the following reversible reaction may be recorded:—



All these considerations are in agreement with those properties of the element arsenic which show it to be more basigenic than phosphorus, and cause it to be classified between the non-metals and metals, as a metalloid.

**Antimonious oxide**,  $\text{Sb}_4\text{O}_6$ , is a crystalline solid which is isodimorphous with arsenious oxide. It is very slightly soluble in water. The hydroxide,  $\text{Sb}(\text{OH})_3$ , manifests both basic and acidic properties, since it is precipitated from solutions of its salts by alkali hydroxide and redissolved by excess. The hydroxide easily loses water, passing into the crystalline oxide.

This behaviour recalls that of arsenious oxide, though arsenious hydroxide has not been obtained, probably because it is not basic enough to be precipitated from solution by alkali.

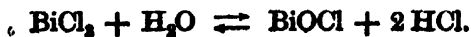
In addition to orthoantimonious acid,  $\text{Sb}(\text{OH})_3$ , which has been obtained pure, the pyroacid,  $\text{Sb}_2\text{O}(\text{OH})_4$ , is likewise known, but the meta-acid,  $\text{SbOOH}$ , has not been obtained in the free state, although the antimonites correspond to it.

Antimonious oxide would be expected to be more basic than arsenious oxide. In accordance with this expectation it is found that antimonious chloride,  $\text{SbCl}_3$ , is a low-melting solid, soluble in non-hydroxylic solvents, which in the liquid state boils at  $223^\circ$ . It is decomposed by water, forming the solid oxychloride,  $\text{SbOCl}$ , known as antimonyl chloride, and this when boiled with excess of water yields the oxide.  $\text{SbCl}_3$  forms various complex salts with the alkali chlorides. The superior basic properties of antimonious oxide are shown in the formation of a crystalline sulphate which separates in needles from a sulphuric-acid solution of  $\text{Sb}_2\text{O}_3$ . A nitrate of somewhat indefinite composition is also known.

**Bismuthous oxide**,  $\text{Bi}_2\text{O}_3$ , usually occurs as a pale-yellow powder, but when crystalline it is isodimorphous with the two preceding oxides. It is much more basic than antimonious oxide, and indeed possesses no perceptibly acidic properties, since the hydroxide, precipitated from solution by potash or ammonia, is not soluble in excess of alkali.

**Bismuthous halides** are feeble salts which melt at comparatively low temperatures and can be distilled. Their halanhydride character is shown by their solubility in non-hydroxylic solvents and their formation of complex halacids and alkali salts. Bismuthous iodide, for instance, dissolves in hydriodic acid, forming hydriodobismuthous acid,  $\text{HBiI}_4 \cdot 4\text{H}_2\text{O}$ —the potassium salt of which crystallizes in red laminae.

The feebly saline character of these halides is manifested by their decomposition by excess of water. Thus the chloride undergoes the following well-known reaction with water, bismuthyl chloride being precipitated:—



$\text{BiOCl}$  is, however, stable towards water, and thus differs from  $\text{SbOCl}$ , which yields the hydrated oxide by further treatment. In this respect bismuth further shows its more metallic character.

The basic nature of bismuthous oxide is best shown by the formation of oxysalts. In addition to the crystalline nitrate,  $\text{Bi}(\text{NO}_3)_3 \cdot 5 \text{H}_2\text{O}$ , which yields a basic salt with water, a basic carbonate, a sulphate, and a phosphate are known. The sulphate forms with potassium sulphate the well-defined double salt  $\text{KBi}(\text{SO}_4)_2$ .

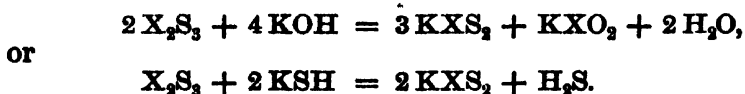
#### SULPHIDES OF THE TYPE $\text{X}_2\text{S}_3$

The comparison of the sulphides of the elements of a natural group with the corresponding oxides constitutes an important study in chemical analogy, since the progression from acidic to basic functions in the oxides finds a parallel in the corresponding sulphides; and nowhere can this parallel be traced better than in the three elements under consideration.

Arsenious, Antimonious, and Bismuthous sulphides are all precipitated from slightly acid solutions of their salts by hydrogen sulphide; but whereas the two former sulphides are soluble in dilute alkali hydroxide and sulphide solutions, bismuth sulphide is insoluble in these reagents, just as bismuth oxide is insoluble in alkali. Thus the fact upon which the analytical separation of these elements is based finds an explanation in accordance with the periodic law.

Bismuthous sulphide is, however, somewhat soluble in concentrated sodium-sulphide solution, but is reprecipitated on dilution; unstable compounds of bismuth sulphide with alkalis can also be obtained by fusion.

The reactions which take place in the solution of the above sulphides may be represented as follows:—



The analogy between the oxides and sulphides is at once seen. When alkali hydroxide is used to dissolve the sulphide a

mixture of thio- and oxysalt is formed; when alkali hydrosulphide is used, thiosalt only results. These sulphides are therefore thioanhydrides which combine with basic sulphides to form metathiosalts.

Whilst bismuth is differentiated from arsenic and antimony by the non-formation of the above compounds, arsenic and antimony may be distinguished, and the more metallic character of the latter manifested, by the following facts:—Although arsenic and antimony sulphides are both easily soluble in potassium-hydroxide solution, antimonious sulphide is less soluble than arsenious sulphide in the weaker base, ammonia; and by the use of a still weaker alkali, namely, ammonium carbonate, these two elements may be separated, since whilst arsenious sulphide dissolves in this reagent, antimonious sulphide is insoluble. The method of separation of arsenic and antimony, depending on the insolubility of arsenious sulphide in concentrated hydrochloric acid, also has significance in this connection, since this fact illustrates the greater difficulty with which arsenic assumes basic functions as compared with antimony.

#### OXIDES OF THE TYPE $X_2O_4$

It will be remembered that  $N_2O_4$  is a mixed anhydride forming nitrous and nitric acids with water, and that  $P_2O_4$  similarly forms phosphorous and phosphoric acids. If intermediate oxides are sought among metals, which may present some analogies to this type, they may be found in  $Fe_3O_4$ ,  $Pb_3O_4$ ,  $Mn_3O_4$ , &c.; and these oxides are salts. With these considerations in view the properties of  $Sb_2O_4$  and  $Bi_2O_4$  may be mentioned.

**Antimony tetroxide,  $Sb_2O_4$ .**—This oxide, which like  $Mn_3O_4$  is formed when either of the other oxides is strongly heated in the air, is sometimes considered to be antimonious ortho-antimonate,  $Sb \cdot SbO_4$ ; it, however, forms the salt  $K_2Sb_2O_6$  when fused with potash, and is therefore more probably hypo-antimonic anhydride.

Corresponding to  $Sb_2O_4$  are complex salts of the type  $M'_2SbCl_6$  derived from the unknown  $SbCl_4$ .

**Bismuth tetroxide,  $Bi_2O_4$ ,** is formed by leading chlorine into

boiling potash solution in which  $\text{Bi}_2\text{O}_3$  is suspended; if too large an excess of potash is present, potassium bismuthate is formed. The compound  $\text{Bi}_2\text{O}_4$  is perhaps bismuthyl bismuthate,  $(\text{BiO})\text{BiO}_3$ .

#### OXIDES OF THE TYPE $\text{X}_2\text{O}_5$

The three oxides,  $\text{As}_2\text{O}_5$ ,  $\text{Sb}_2\text{O}_5$ ,  $\text{Bi}_2\text{O}_5$ , manifest the properties of acidic anhydrides,  $\text{Bi}_2\text{O}_5$  also behaving as a basic peroxide like  $\text{PbO}_2$ .

✓ **Arsenic pentoxide**,  $\text{As}_2\text{O}_5$ , resembles phosphoric oxide in dissolving in water to form a strongly-acid solution containing  $\text{H}_3\text{AsO}_4$ ; and it is obtained as a glassy mass by careful ignition of this acid. When strongly heated, unlike phosphorus pentoxide, it breaks up into oxygen and the trioxide, and hence its vapour density has not been determined. Again, whilst phosphorus burns directly to the pentoxide, arsenic produces the trioxide when burnt. Nitrogen pentoxide, prepared by the dehydration of nitric acid, is easily decomposed by heat. )

It is therefore seen that the tendency towards complete oxidation, in which phosphorus exceeds nitrogen, and which is so characteristic of the former element, diminishes again with arsenic. Otherwise arsenic closely resembles phosphorus in its most highly oxidized compounds. The three products of hydration of arsenic oxide, viz.,

Metarsenic acid  $\text{HAsO}_3$ ,  
Pyroarsenic acid  $\text{H}_4\text{As}_2\text{O}_7$ ,  
Orthoarsenic acid  $\text{H}_3\text{AsO}_4$ ,

are analogous and very similar to those of phosphoric oxide.

The meta<sup>2</sup> and pyro-acids, however, are rather less stable towards water than the corresponding acids of phosphorus; metarsenic acid yields the anhydride on ignition, while metaphosphoric acid is stable.

A solution of arsenic acid, obtained by oxidation of arsenious oxide with nitric acid, deposits crystals of the hydrate  $\text{As}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$  which effloresce in a dry atmosphere forming  $\text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ , which is pyro-arsenic acid,  $\text{H}_4\text{As}_2\text{O}_7$ . Baud<sup>1</sup> therefore regards  $\text{As}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$  as a hydrate of the pyro-

<sup>1</sup> *Compt. rend.*, 1907, 145, 822.

acid, so that the solid ortho-acid,  $\text{H}_3\text{AsO}_4$ , appears not to exist.

When pyro-arsenic acid is strongly heated it yields first metarsenic acid; then the anhydride, which finally breaks up into arsenious oxide and oxygen, as previously stated.

The close analogy between phosphoric and arsenic acids and their derivatives is seen in the consideration of the following facts:—

$\text{Na}_2\text{HPO}_4, 12\text{H}_2\text{O}$  is isomorphous with  $\text{Na}_2\text{HAsO}_4, 12\text{H}_2\text{O}$ ,  
 $\text{MgNH}_4\text{PO}_4, 6\text{H}_2\text{O}$  is isomorphous with  $\text{MgNH}_4\text{AsO}_4, 6\text{H}_2\text{O}$ .

Ammonium phosphomolybdate is similar to ammonium arseni-molybdate, though the latter is formed with somewhat more difficulty at a higher temperature than its phosphorus analogue.

**Antimony pentoxide**,  $\text{Sb}_2\text{O}_5$ , obtained by the action of nitric acid on the metal, is a light-yellow powder, practically insoluble in water, though it manifests an acid reaction towards litmus. It forms ortho-, pyro-, and meta-antimonic acid, but the principal salts exist in the meta form.

The oxide is fairly stable, breaking up at high temperature into the tetroxide and oxygen.

**Bismuth pentoxide**,  $\text{Bi}_2\text{O}_5$ , is an unstable brown powder obtained by the gentle ignition of bismuthic acid,  $\text{HBiO}_3$ . This latter substance is precipitated as a red powder when chlorine is passed through boiling caustic-potash solution containing bismuthous oxide in suspension; it possesses very feebly acidic properties, as is shown by its method of preparation, and forms unstable salts with alkalis, which are decomposed by water. With hydrochloric and oxyacids it yields bismuthous salts and chlorine or oxygen, thus behaving as a basic peroxide, owing to the instability of bismuthic compounds.

#### PENTAHALIDES OF ARSENIC AND ANTIMONY

It was pointed out when studying phosphorus that phosphorus pentachloride is less stable than the pentoxide, as is manifested in the dissociation of the former by heat. Now since arsenic pentoxide is itself dissociated by heat, it is to be expected that the pentahalides of this element will be very

unstable. This is the case, arsenic pentachloride being unknown, though the iodide has been obtained.

Antimony pentoxide, on the other hand, is more stable than arsenic pentoxide, and (antimony pentachloride is a yellow fuming liquid prepared from the trichloride and chlorine, and sufficiently stable to be distilled under reduced, but not under normal pressure. Its chemical nature may be judged from the fact that it forms a crystallohydrate with ice-cold water, but is decomposed by hot water into antimonious and hydrochloric acids. Its behaviour is thus analogous to that of stannic chloride, just as antimony is comparable with tin in metallic properties.

Bismuth pentachloride is not known, and would not be expected to exist, considering the instability of the pentoxide.

#### PENTASULPHIDES

The pentasulphides of arsenic, antimony, and bismuth all exist.

**Arsenic pentasulphide**,  $\text{As}_2\text{S}_5$ , is formed as a yellow precipitate when hydrogen sulphide is passed through arsenate solution to which much hydrochloric acid has been added, so that  $\text{AsCl}_5$  is present. In the absence of much acid, arsenate is first reduced more or less to arsenite, and consequently  $\text{As}_2\text{S}_3$  is precipitated.  $\text{As}_2\text{S}_5$  is also formed in the dry way, and may be sublimed. It is a thioanhydride, dissolving in alkalis according to the following reaction:—



If alkali sulphide is employed, thioarsenate,  $\text{M}_3\text{AsS}_4$ , alone results. The free acid is liberated by acidifying a thioarsenate solution, but quickly decomposes, giving a precipitate of the pentasulphide.

Salts of meta- and pyro-, as well as of orthothioarsenic acid, are known.

**Antimony pentasulphide**,  $\text{Sb}_2\text{S}_5$ , is more stable than  $\text{As}_2\text{S}_5$ , being formed as a red precipitate when hydrogen sulphide is passed into a slightly acidified solution of an antimonate.

**Bismuth pentasulphide**,  $\text{Bi}_2\text{S}_5$ , is black, and manifests no acidic properties, not being soluble in alkalis.



## THE ELEMENTS OF SUB-GROUP V A

*Vanadium, Niobium (Columbium), Didymium, and Tantalum*

Of the elements of this sub-group, vanadium is of interest on account of the number of types of compound which it forms. In this it shows analogy with nitrogen, and especially with phosphorus, although it differs from these elements by reason of its distinctly metallic properties. Didymium presents a curious phenomenon from the point of view of the periodic law, since it consists of two elements whose atomic weights lie close together. Niobium and tantalum are rare elements; the latter is used for making the filaments of electric lamps.

## VANADIUM

This element was obtained by Roscoe by heating the dichloride in an atmosphere of pure hydrogen. It is a whitish-grey crystalline powder which does not melt nor volatilize when heated to redness in hydrogen. It thus presents a marked contrast to arsenic, its analogue in sub-group B. Its feebly metallic properties are shown by the fact that it does not displace hydrogen from water or dilute acids except from hydrofluoric acid. It readily absorbs and combines with oxygen and nitrogen when heated in these gases.

Vanadium resembles nitrogen in forming the complete series of oxides,  $V_2O$ ,  $V_2O_2(VO)$ ,  $V_2O_3$ ,  $V_2O_4(VO_2)$ ,  $V_2O_5$ .

**Vanadium monoxide**,  $V_2O$ , is a neutral oxide, similar to the lower oxides of molybdenum and tungsten, which do not fulfil their expected basic function, being insoluble in acids.

**Hypovanadious oxide**,  $V_2O_2$ , or  $VO$ , was mistaken by Berzelius for the metal. A chloride and sulphate are known, the latter forming with potassium sulphate the double salt,  $VSO_4$ ,  $K_2SO_4$ ,  $6H_2O$ .

**Vanadious oxide**,  $V_2O_3$ , is insoluble in acids but its chloride and sulphate are well known, the latter forming true alums with alkali sulphates. Vanadyl monochloride,  $VOCl$ , is a basic salt.

**Hypovanadic oxide**,  $V_2O_4$  or  $VO_2$ , forms hypovanadates, e.g.

$\text{Ag}_2\text{V}_2\text{O}_5$  and  $\text{K}_2\text{V}_4\text{O}_9, 7 \text{H}_2\text{O}$ . A tetrachloride is known, and the following basic salts:  $\text{V}_2\text{O}_2\text{Cl}_4$ ,  $\text{V}_2\text{O}_8\text{Cl}_2$ ,  $\text{V}_2\text{O}_2(\text{SO}_4)_2, 4 \text{H}_2\text{O}$ . In this oxide basic and acidic properties are about equal.

**Vanadic oxide**,  $\text{V}_2\text{O}_5$ , possesses well-developed acidic and feebly basic properties. It is, however, a weak anhydride, and is separated as a red powder from a solution of a salt by addition of acid. This oxide fuses without loss of oxygen. Meta- and pyro-vanadic acids, and meta- as well as tetra- and hexavanadates, exist. These latter salts, which are unrepresented among phosphorus compounds—tetra- and hexameta-phosphates belonging to another category,—are peculiarly characteristic of polybasic acids derived from weak metals or non-metals. Chromium, molybdenum, and tungsten form such acids, as well as boron, among non-metals. Vanadic resembles phosphoric acid in forming complex acids with molybdic and tungstic acids.  $\text{NH}_4\text{VO}_3$  is the best-known vanadate.

The existence of  $\text{VCl}_5$  is doubtful, but  $\text{VOCl}_3$  is a lemon-yellow liquid, boiling at  $126.7^\circ$ , soluble in non-hydroxylic solvents, and decomposed by water. It is an oxychloranhydride rather than a basic salt.

The sulphate  $(\text{VO})_2(\text{SO}_4)_3$  may be obtained from a solution of the oxide in concentrated sulphuric acid. It forms double salts with the alkali sulphates.

It will be seen from the above brief account of vanadium compounds that they manifest all stages from basic to acidic properties with increase in proportion of oxygen; but that, in accordance with the position of the element in the A sub-group, even the most highly oxidized derivatives are basic.

Salts corresponding to the various stages of oxidation possess different colours; those of  $\text{V}_2\text{O}_5$  are yellow, of  $\text{V}_2\text{O}_4$  <sup>1</sup> blue, of  $\text{V}_2\text{O}_3$  green, of  $\text{V}_2\text{O}_2$  lavender. When zinc is placed in an acidified solution of ammonium vanadate, the above colours, with intermediate shades, may be observed as reduction proceeds.

**Pervanadic acid**,  $\text{HVO}_4$ , is deposited as unstable yellow crystals from a deep red solution formed by adding vanadic

<sup>1</sup> The lower oxides of vanadium are powerful reducing agents. A solution of  $\text{V}_2\text{O}_4$  in dilute sulphuric acid serves to standardize permanganate, and after oxidation may be reduced again by  $\text{SO}_2$ .

oxide to a solution of hydrogen peroxide and dilute sulphuric acid. The potassium salt is yellow and microcrystalline.

#### NIBIUM AND TANTALUM

These metals do not readily dissolve in acids. Niobium may be dissolved by concentrated sulphuric acid, and tantalum by hydrofluoric acid, forming pentafluoride in solution. Neither metal can be said to form salts with acids, and the sesquioxides are not known. The remarkable absence of basic oxides in the case of these two metals finds a parallel in the sixth group with molybdenum and tungsten.

**Niobium pentoxide**,  $\text{Nb}_2\text{O}_5$ , is a feebly acidic oxide, forming meta- and polysalts. The halides,  $\text{NbX}_5$ , are volatile, and are halanhydrides, forming complex salts with alkali halides. Oxyhalides,  $\text{NbOX}_3$ , are likewise known.

**Tantalum pentoxide**,  $\text{Ta}_2\text{O}_5$ , possesses similar properties to  $\text{Nb}_2\text{O}_5$ , and forms analogous salts. The pentafluoride forms an important series of complex salts with the alkali fluorides, for instance, potassium fluotantalate or tantalifluoride,  $\text{K}_2\text{TiF}_7$ .

**Perniobates** and **pertantalates** have been obtained by the action of hydrogen peroxide on the alkali niobates and tantalates respectively. They are probably to be regarded as compounds of alkali peroxide with niobic and tantalic oxides, the valency of the metallic atoms of niobium and tantalum not being increased.

#### . DIDYMIUM

This body is included among the metals of the rare earths. Most of these metals appear to belong to Group III, though cerium must be placed in Group IV. The name didymium was originally given to a supposed element discovered by Mosander in 1841, on account of the close relationship of its compounds to those of lanthanum, from which it was separated by this chemist. From didymia, its oxide, a new earth, **samarium**, was isolated by Lecoq de Boisbaudran in 1879; and the residue, which for a time was considered to be the oxide of a single metal, didymium, with an atomic weight about equal to 140, was resolved into two constituents by Auer

von Welsbach in 1835. The purified didymium salts are red or violet, and give a characteristic absorption spectrum when in solution. The oxide is of a dingy blue colour. By fractional crystallization of a nitric-acid solution of a double nitrate of the metal and ammonium, von Welsbach obtained two salts which were bright green and amethyst coloured respectively, and whose oxides were respectively greenish white and pale blue.

The absorption spectra of these salts are distinct from one another, but when their solutions are mixed in suitable proportions the original didymium spectrum is reproduced.

To the supposed elements giving rise to these compounds the names **praseodymium**<sup>1</sup> (Pr) and **neodymium** (Nd) were given, and their atomic weights are respectively

$$\text{Pr} = 140.6$$

$$\text{Nd} = 144.3.$$

The oxides  $\text{Pr}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3$  are entirely basic; an oxide  $\text{Pr}_2\text{O}_5$  is said to exist; the oxide  $\text{Nd}_2\text{O}_4$  is a basic peroxide, decomposing hydrogen peroxide, and liberating chlorine from hydrogen chloride.

The occurrence of two closely allied elements of approximately equal atomic weight, where one only would be expected, presents an interesting and difficult problem from the point of view of the periodic law, and one for which at present there is no solution. The case of nickel and cobalt furnishes some analogy in the chemical relationships and colours of salts.

#### NOTE ON THE FIXATION OF ATMOSPHERIC NITROGEN

A study of the distribution of terrestrial nitrogen shows that this element is present in volcanic gases, and that it exists combined in small quantities in deep-seated nitrides and in surface deposits of nitrates, as well as in accumulations of nitrogenous matter of undoubtedly organic origin. Thus nitrogen appears to form but a very small part of the crust or internal mass of the earth.

This fact is no doubt to be attributed to the inertness of nitrogen, which consequently failed to combine to any extent with other elements in the earlier stages of cosmic development. Some of this free cosmic nitrogen was probably originally occluded within the generating material of our planet, and eventually accumulated outside the earth forming the larger part of our atmosphere.

Notwithstanding the comparative rarity of combined nitrogen, this element plays an essential part in vegetable and animal metabolism, since it enters into the composition of the numerous and important class of proteins.

How nitrogen has become available for plant and animal life, and how its availability may be increased artificially, are questions which will here be dealt with.

Plants require nitrogenous food in the form of soluble nitrate; and this material results naturally from atmospheric electric discharge, whereby nitric acid is formed. In this way about eleven pounds of nitrate per acre are annually formed in the temperate, and a larger amount in the tropical regions. This, however, is not the only means by which atmospheric nitrogen is fixed.

Nodules found on the roots of leguminous plants consist of colonies of *azoto bacteria*, which in symbiotic union with these plants enable them directly to assimilate atmospheric nitrogen.

Rotation of crops, justified by long experience, depends on the enrichment of exhausted soil by a leguminous crop.

Thus, firstly by electric discharge, and secondly by the aid of certain micro-organisms, atmospheric nitrogen is made available for plant, and thence for animal food.

Simultaneously, however, some nitrogen is being yielded back to the air by organic decay, and the work of denitrifying bacteria; but the currency of most of the fixed nitrogen is upheld through the agency of *nitrifying bacteria*.

Animal waste nitrogen is eliminated chiefly in the form of urea, of which it has been calculated that about 40,000 tons per day are produced by mankind alone. In the soil urea is hydrolysed to ammonium carbonate, and the ammonia of this

salt is converted first to nitrite and eventually to nitrate by nitrifying bacteria. This is a natural process, which is employed, and can be followed readily in the course of sewage purification. Nitrates are the final products of natural purification, and are also the most available nitrogenous plant foods.

Under conditions of artificial cultivation, but especially by reason of sewage disposal systems rendered necessary by the congestion of population, animal nitrogenous waste is very largely diverted from the soil to the sea. This is perhaps the most serious cause of depletion of the soil of nitrogen; for unless nearly all the animal waste resulting from the use of nitrogenous vegetable food is returned to the soil, local impoverishment must occur. It thus becomes needful to supply artificial nitrogenous manures, of which the main sources are:—

(a) Guano, which is limited in quantity, is not the most available form, and is practically exhausted.

(b) Ammonia in the form of sulphate, derived from the distillation of shale and from the manufacture of coal gas and Mond gas.

(c) Chili saltpetre, or sodium nitrate.

Now all these sources of nitrogenous manure are limited. The total annual production of ammonium sulphate in this country is about 300,000 tons; the total exportation of Chili saltpetre in 1908 was 2,200,000 tons, and the estimated amount of the deposits is variously quoted as from 50 to 120 millions of tons.

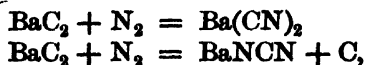
The possibility of the nitrogen starvation of the vegetable kingdom within a generation or two therefore becomes a matter of the vastest economic significance.

In the atmosphere there are about 4000 billion tons of nitrogen; or otherwise, over 1000 acres there is nitrogen equivalent to nearly 200 millions of tons of Chili saltpetre, or nearly twice the estimated amount in the beds. Yet by reason of the relative inertness of nitrogen the problem of fixing this element by chemical methods at a price to compete with ammonia and saltpetre is one of great difficulty.

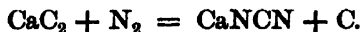
At present the chemical fixation of atmospheric nitrogen

can only be carried out commercially where a natural head of water affords cheap motive power. The two processes employed are: the formation of calcium cyanamide,  $\text{CaNCN}$ , by absorption of nitrogen by calcium carbide (Caro); and the formation of nitric oxide, subsequently converted into nitric acid, by the action of the electric arc on air (Birkeland-Eyde). Both processes depend on the generation of electricity by water power, and are at present chiefly operated in Norway and Sweden, though cyanamide manufacture is projected in other European countries, in America, and in the East.

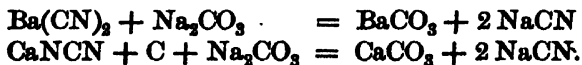
**The Cyanamide Process.**—The union of acetylene and nitrogen to form hydrocyanic acid was demonstrated by Berthelot in 1869. Carbides of barium and calcium, whose preparation we owe to Moissan, similarly unite with nitrogen at high temperatures, but only when impure, to yield in the case of barium a mixture of cyanide and cyanamide:—



and in the case of calcium, cyanamide only:—



Each of these derivatives yields sodium cyanide, and the alkaline-earth carbonate, on fusion with sodium carbonate:—



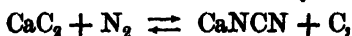
Under the names of "calcium cyanamide", "kalkstickstoff", or "nitrolim", the calcium compound is now produced commercially.

The preparation of "nitrolim" requires pure nitrogen. In the factories at Odda, in Norway, atmospheric nitrogen is separated from the air by means of a Linde liquefying plant, advantage being taken of the boiling-point difference between nitrogen,  $= -196^\circ \text{C}$ ., and oxygen,  $= -183^\circ \text{C}$ .

As alternative processes for obtaining nitrogen, air may be passed over hot copper, the oxide being subsequently reduced by generator gas; or producer gas ( $\text{N}_2$ ,  $\text{CO}$ ,  $\text{O}_2$ ) may be passed

over a hot mixture of copper and its oxide, whereby a mixture of nitrogen and carbon dioxide is formed (Caro).

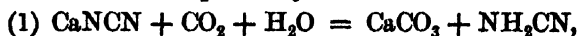
The reaction of formation of calcium cyanamide,



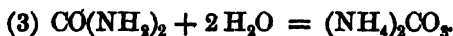
begins at 800° to 900° C., and is reversible above 1000° C. Admixture of calcium chloride or fluoride facilitates the reaction probably by lowering the fusion temperature.

The use of cyanamide as a fertilizer depends on the formation by hydrolysis of ammonia, which is eventually converted into nitrate by the nitrifying organisms of the soil.

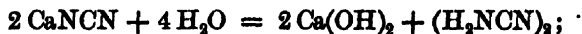
The former reactions probably are:—



the urea thus formed is hydrolysed (by the hydrolytic micrococcus of urea) to ammonium carbonate:



Other applications of nitrolim are: the formation of ammonia by means of superheated steam; the formation of nitric acid by oxidation under the catalytic influence of platinum (Ostwald), or a mixture of thoria and ceria (Frank and Caro); the formation of cyanides,  $\text{CaNCN} + \text{C} \rightleftharpoons \text{Ca}(\text{CN})_2$ , by heating with a suitable flux; the formation of dicyandiamide by the action of cold water,



and the production of urea,  $\text{CO}(\text{NH}_2)_2$ , of guanidine,  $\text{NH}:\text{C}(\text{NH}_2)_2$ , and of nitroguanidine,  $\text{NO}_2\text{N}:\text{C}(\text{NH}_2)_2$ , by the action of acids.

**The Atmospheric Nitric Acid Process.**—The direct union of oxygen and nitrogen with the formation of nitric oxide, in accordance with the reversible reaction:



either under the influence of the electric discharge, or at the temperature of a hot flame such as that of hydrogen, has long been known, having first been observed by Priestley and by Cavendish.



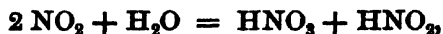
Nitric oxide is endothermic, and unstable above  $1200^{\circ}$ ; at  $3200^{\circ}$  about 5 per cent by volume can be formed from air, and about 14 per cent from an equimolecular mixture of oxygen and nitrogen. Owing, however, to the difficulty of rapidly cooling the gases from the temperature of the electric arc (about  $3000^{\circ}$  to  $3500^{\circ}$ ) to below the stability temperature ( $1200^{\circ}$ ), the actual yields of oxide do not exceed 1.5 to 2 per cent of the volume of air employed.

As with nitrolim, the process can only be conducted commercially when accessible water power supplies cheap electric energy.

Two main types of arc flame are in use to-day at the Norwegian works at Notodden. That of Birkeland and Eyde is an alternating-current arc formed between copper poles in a powerful magnetic field, which, on account of the attraction of the arcs by the electro-magnet, presents the appearance of a disk of flame. In reality the positive and negative arcs are rapidly attracted in opposite directions to the limit of the disk, when they are broken and a fresh one is produced, the succession being so rapid that the visible result is that of the disk.

In the Schönherr arc a long flame is produced in a relatively narrow iron tube, through which the air also passes. Having a rotary motion as it enters the tube, the air current assists in elongating the arc formed in the first instance between the inner pole and the wall of the tube, which is earthed and constitutes the other pole. Arcs as long as 8 yards may thus be formed; and although the gases are in contact with the flame for this length, the yield of oxide appears to be greater than with the Birkeland-Eyde flame.

On leaving the furnaces the gases have a temperature of from  $800^{\circ}$  to  $1000^{\circ}$ , and are rapidly cooled, the heat removed from them sufficing for purposes of steam generation and evaporation. Union of nitric oxide and oxygen begins below  $500^{\circ}$ , and at  $50^{\circ}$ , to which the gas is finally reduced, it contains 2 per cent of nitrogen peroxide. On absorption by water a mixture of nitric and nitrous acids is formed:



but nitrous acid rather easily undergoes self-oxidation and reduction, especially in higher concentration, thus:

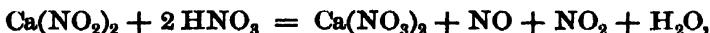


and the nitric oxide with a fresh quantity of oxygen again yields  $\text{NO}_2$ , so that the greater part of the peroxide is converted eventually into nitric acid.

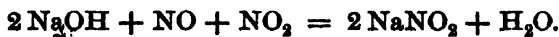
Absorption is effected in a series of towers in which the water passes in the opposite direction to the gas current, so that acid of about 50 per cent strength is formed in the first tower, whilst nitrous acid tends to be formed in the last. An additional tower, containing milk of lime, effects the removal of the last traces of oxides, in the form of calcium nitrite and a little nitrate.

The acid may be concentrated by distillation with sulphuric acid, or it may be neutralized with chalk and the solution evaporated till crystallized calcium nitrate,  $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ , separates; or the liquid may be still further concentrated until it sets to a hard mass, forming the "Norwegian saltpetre" or "air saltpetre" of commerce.

Nitrites are obtained from the product in the last tower. If calcium nitrite has been made, "nitrous fumes" are produced by the action of nitric acid:



and on absorption by caustic soda give technically pure nitrite,



Such are the purely chemical methods by which the problem of the fixation of nitrogen has been solved. Attempts to find a solution on biological lines have been numerous, and are still *sub judice*. The application to the soil of pure cultures of the nitrogen-assimilating organism appears a rational method. So far, however, it does not seem that such applications have led to marked improvement in the total nitrogen of experimental crops.

## NOTE ON LIQUID AMMONIA AS A SOLVENT

In various reactions ammonia is analogous to water, as in the formation of alkali and acidic amides from alkali metals and acidic chlorides respectively, as well as of imides from the amides of dibasic organic acids by loss of ammonia. Thus it is suggested that the amide group ( $\text{'NH}_2$ ) is analogous to hydroxyl ( $\text{'OH}$ ), whilst the imide group ( $\text{'NH}$ ) is analogous to oxide ( $= \text{O}$ ).

This analogy may be further developed.

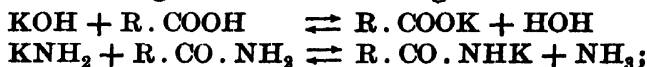
OH attached to metal gives an oxybase, *e.g.* KOH,

$\text{NH}_2$  attached to metal gives an **ammonobase**, *e.g.*  $\text{KNH}_2$ ,

OH attached to an acidic group gives an oxyacid, *e.g.*  $\text{R} \cdot \text{COOH}$ ,

$\text{NH}_2$  attached to an acidic group gives an **ammonoacid**, *e.g.*  $\text{R} \cdot \text{CO} \cdot \text{NH}_2$ .

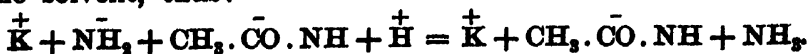
Hence the following reactions are analogous:—



that is to say, analogous to oxysalt formation and hydrolysis there are **ammonosalt formation** and **ammonolysis**. Just as the oxy-reactions are realizable through the agency and medium of liquid water, so the analogous ammono-reactions take place in liquid ammonia; this has been shown by Franklin and his co-workers, to whom both the reactions and the nomenclature are due.<sup>1</sup>

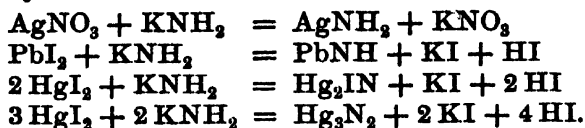
Anhydrous liquid ammonia, which boils at  $-38.5^\circ$ , resembles water in being itself a non-electrolyte, and a good solvent and ionizing medium.

If potassamide is dissolved in liquid ammonia containing phenolphthalein, the colourless liquid turns red owing to the presence of alkali. The ammonobase  $\text{KNH}_2$  has been ionized, and the alkalinity must be due to  $\text{NH}_2$  ions. The colour of the indicator is discharged by the addition of acetamide,  $\text{CH}_3 \cdot \text{CO} \cdot \text{NH}_2$ , an ammonoacid, whose H ions unite with  $\text{NH}_2$  ions to produce ammonia, which becomes part of the solvent, thus:



<sup>1</sup> *J. Amer. Chem. Soc.*, 1906, 27, 820-51.

Reactions of precipitation can also be carried out in the same medium; *e.g.*:



Silver amide,  $\text{AgNH}_2$ , and lead imide,  $\text{PbNH}$ , are new substances; the nitrogenous mercury compounds have been obtained in other ways (see p. 134).

## CHAPTER X

## GROUP VI

## SUB-GROUP A

: O (16·00)  
: S (32·07)

Cr (52·0)

Mo (96·0)

W (184·0)

U (238·5)

## SUB-GROUP B

Se (79·2):

Te (127·5)

The sub-groups A and B respectively form families of closely related elements, in both of which the change of chemical character is from less to more basigenic. Whilst the members of sub-group B are oxygenic, signs of a basigenic character first appearing in tellurium, the elements of the A sub-group are basigenic\* or metallic, acidic characters being displayed only in compounds containing a large proportion of a non-metallic element, such as the trioxides,  $\text{MO}_3$ , which show acidic properties, diminishing in degree from chromium to uranium.

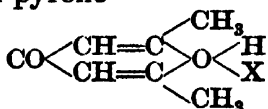
As would be expected, from principles of the periodic law previously considered, the relationship between sub-groups A and B is somewhat remote; but the maintenance of the group-type by the formation of a series of acidic trioxides clearly reveals such similarity as justifies the inclusion of all these elements in one group. As in the case of other groups,

hydrides and volatile alkyl compounds are only formed by the members of the B sub-group.

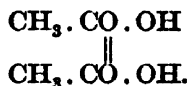
The maximum halogen valency of Group VI is six, the type being represented, however, only by  $\text{MoF}_6$ ,  $\text{WF}_6$ ,  $\text{WCl}_6$ , and  $\text{SF}_6$ . Other halogen valencies, 2, 3, 4, and 5, are all represented. The oxygen valency is also six, and is represented by the highest normal oxides,  $\text{MO}_3$ . Oxygen almost invariably behaves as divalent, but the existence of such compounds as



and salts of dimethyl pyrone



indicates the tetravalency of this element, these oxonium compounds resembling the trialkyl salts of sulphur,  $\text{R}_3\text{SX}$ , the sulphonium salts. In this type oxygen appears to possess basic properties, but in the majority of its other combinations it confers acidic properties, the higher oxides of an element, for example, being more acidic than the lower. Further examples of the probable tetravalency of oxygen are furnished by the double water molecules,  $\text{H}_2\text{O} = \text{OH}_2$ , which are believed to exist in the liquid state, as well as by double acetic acid molecules,



The combination of water of crystallization in salts is explained by some chemists on the theory of the tetravalency of oxygen.

#### SUB-GROUP VIB,

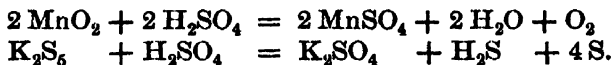
Oxygen, sulphur, selenium, and tellurium all form binary compounds with metals from which acids liberate the hydrides  $\text{H}_2\text{X}$ . The occurrence of these elements in nature in the form of such metallic compounds<sup>1</sup> illustrates the analogy between them.

<sup>1</sup> E.g.  $\text{Cu}_2\text{O}$ ,  $\text{Cu}_2\text{S}$ ;  $\text{HgO}$ ,  $\text{HgS}$ ;  $\text{Sb}_2\text{O}_3$ ,  $\text{Sb}_2\text{S}_3$ ;  $\text{PbS}$ ,  $\text{PbSe}$ ;  $\text{HgSe} + 4\text{HgS}$ ;  $\text{Ag}_2\text{S}$ ,  $\text{Ag}_2\text{Te}$ ;  $\text{Bi}_2\text{O}_3$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{Bi}_2\text{Te}_3$ .

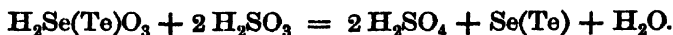
A comparable mode of preparation of the elements is furnished by the decomposition of the hydrides either by heat or, in the case of oxygen, by electrolysis. Other comparable methods for oxygen and sulphur are the heating of the higher oxides or sulphides, as for example:



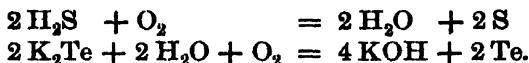
and the decomposition of similar compounds by acids, *e.g.*:



Selenium and tellurium result from the reduction of selenious and tellurous acids by sulphurous acid:




Selenium, tellurium, and sulphur are liberated when their hydrides or metallic compounds are decomposed by oxygen:



Some physical properties of these elements are here given:

		Colour.	M.P.	B.P. (1 atm.)	Allotropic Forms.
<b>Oxygen...</b>	Gas	Colourless	-223° (O <sub>2</sub> )	{ -182.5° (O <sub>2</sub> ) -119° (O <sub>3</sub> ) }	O <sub>2</sub> and O <sub>3</sub> (Ozone) <sup>1</sup>
<b>Sulphur..</b>	Solid	Yellow	{ 114.5° (rhombic) 119.25° (monoclinic) }	448.4°	{ Rhombic Monoclinic Amorphous
<b>Selenium</b>	Solid	Red or black	217°	680°	{ Red crystalline Black amorphous Black crystalline } soluble in C <sub>2</sub> insol. in C <sub>2</sub>
<b>Tellurium</b>	Solid	{ Greyish or silvery white }	452°	478° in vacuo	{ Crystalline Amorphous (unstable) by precipitation }

<sup>1</sup> Ozone is formed from oxygen when disruption of O<sub>2</sub> molecules takes place under conditions favouring condensation to O<sub>3</sub> molecules.

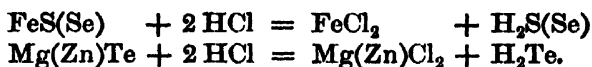
In the electrolysis of dilute H<sub>2</sub>SO<sub>4</sub> with a minute anode of platinum foil, the evolved oxygen may contain 23 per cent of ozone (Fischer and Bendixsohn, *Zeit. Anorg. Chem.*, 1909, 61, 13); and when a silent discharge is passed through oxygen at the temperature of liquid air, 99 per cent of the gas is converted into ozone (Briner and Durand, *Compt. rend.*, 1907, 145, 1272). The stability of ozone diminishes with rise of temperature, and at 300° it is completely re-converted into oxygen. Ozone differs from hydrogen peroxide, which otherwise, as an oxidising agent, it much resembles, in not reacting with chromic acid. It combines with certain unsaturated organic compounds, *e.g.* turpentine, to form ozonides. Ethylene ozonide is O<sub>3</sub> .

The gradation of properties—setting aside oxygen, which as the first member of the series may be expected to be anomalous—will be seen to accord with that demanded by the periodic law. It will be noted further, that allotropy is less well defined with tellurium than with selenium and sulphur; this is in harmony with the increased positive character of the former element.

#### HYDRIDES

The hydrides,  $\text{XH}_2$ , all result from the direct union of the elements, the ease of combination diminishing from oxygen to tellurium, decrease of non-metallic character being thus exhibited. Hydrogen and sulphur combine directly at about  $400^\circ$ , hydrogen and selenium at about  $500^\circ$ .

The oxides, sulphides, selenides, and tellurides of many metals (particularly those which give hydrogen with dilute acid), which have been produced by the direct union of the elements, yield hydrides by the action of acids; thus:—



With the exception of water they are all gases at ordinary temperature; they can, however, be liquefied and solidified with moderate ease, as the following figures show:—

	$\text{H}_2\text{S}$	$\text{H}_2\text{Se}$	$\text{H}_2\text{Te}$
Boiling-point at atm. press. ....	$-61.8^\circ$	$-42^\circ$	$0^\circ$
Melting-point.....	$85^\circ$	$-64^\circ$	$-48^\circ$

The boiling and melting points rise considerably in passing from sulphur to tellurium. The behaviour of water is seen to be anomalous; and is probably accounted for, as previously suggested, by polymerization.

The variation of properties in a regular manner is shown in several ways. Thus, the heats of formation are:—



Parallel therewith, it is noticed that the ease of dissociation by heat increases with rise of molecular weight. Whilst water

first dissociates at nearly 2000°, hydrogen sulphide is decomposed at 400–600°, and hydrogen selenide and telluride are resolved into their elements at lower temperatures (about 150°) than those at which they are produced by direct union, so that when the elements are heated below their boiling-points in a closed tube of hydrogen, crystalline sublimates are formed on the cooler parts of the tube.

Further, just as oxygen displaces sulphur from hydrogen sulphide, so sulphur displaces selenium from hydrogen selenide. And similarly, a reaction in the sense of the equation



occurs far more readily with hydrogen sulphide than with water.

The hydrides of sulphur, selenium, and tellurium display feebly acidic properties, and react with solutions of metallic salts, yielding sulphides, selenides, and tellurides respectively. The position of water in this respect appears at first sight to be anomalous. Water behaves as a neutral oxide, and is described as *amphoteric*. As the first of the series of hydrides, it would be expected from analogy to be the most basic or least acidic, and such is actually the case. In a comparison of the properties of the hydrides of the fifth group, it was found that whilst ammonia is basic, and phosphine practically neutral, acidic properties begin to appear with the hydrides of arsenic and antimony, inasmuch as an unstable arsenide and a more stable antimonide are formed when these gases react with silver-nitrate solution. Now in chemical properties water bears approximately the same relation to phosphine as sulphuretted hydrogen does to arsine; in each case there is a slight diminution of basic properties in passing from the fifth to the sixth group. It was further observed that the basic properties of the hydrides of the fifth group are increased by substitution of alkyl groups for hydrogen. The same fact is observable in the sixth group, since methyl oxide<sup>1</sup> combines with hydrogen chloride to form dimethyloxonium chloride,

<sup>1</sup> This might be called dimethyloxine, water itself being oxine.



$O(CH_3)_2HCl$ , previously mentioned, a derivative of the hypothetical oxonium radicle  $(OH_3)'$ ; derivatives of hydrogen sulphide give rise to the sulphonium compounds,  $SR_3A$ , whilst selenonium compounds are similarly derived from hydrogen selenide.<sup>1</sup> It will appear from these considerations that the neutral properties of water are to be expected from the periodic law; and even the condensibility of this compound, and the existence of complex molecules in the liquid state, find a parallel in the case of hydrogen fluoride, its neighbour in the seventh group.

#### HALIDES

These are of several types:—

	F'	Cl'	Br'	I'
$X_2R_2$ .....{	— —	$S_2Cl_2$ $Se_2Cl_2$ ✓	— $S_2Br_2$	$S_2I_2$ $Se_2I_2$ ✓
$XR_2$ .....{	— —	$SCl_2$ $TeCl_2$ ✓	— $TeBr_2$ ✓	— $TeI_2$ ✓
$XR_4$ .....{	— —	$SCl_4$ $SeCl_4$ ✓	— $SeBr_4$ ✓	— $SeI_4$ ✓
	$TeF_4$ ✓	$TeCl_4$ ✓	$TeBr_4$ ✓	$TeI_4$ ✓
$XR_6$ .....	$SF_6$	—	—	—

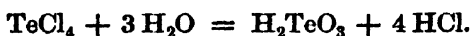
The inclusion of the oxygen compounds of the halogens among the halides of Group VI is not warranted, for whilst the typical halides of this group are halanhydrides corresponding with certain oxyacids, the oxygen compounds  $Cl_2O$ ,  $ClO_2$ ,  $I_2O_5$ , and  $I_2O_7$  are anhydrides of the halogen oxyacids, and are therefore dealt with under Group VII.

The Group VI halides result in general from direct union of the elements, the type of halide produced depending on the relative proportions of the reacting substances and the conditions of the experiment. <sup>†</sup>Sulphur monochloride, for instance, is stable, and can be distilled; by the action of chlorine upon it the unstable dichloride is formed, and may be distilled under low pressure; and by the further action of chlorine at  $-22^\circ$  the unstable tetrachloride results.

<sup>1</sup> See also Iodonium compounds, p. 301.

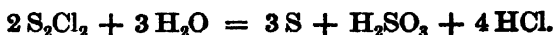
**Sulphur hexafluoride**,  $\text{SF}_6$ , formed by the combination of its elements, is a colourless stable gas. **Selenium** first yields a **monochloride**,  $\text{Se}_2\text{Cl}_2$ , by the action of chlorine; it gives no dichloride, but its **tetrachloride** can be distilled. **Tellurium** forms the **dichloride** and stable **tetrachloride**, the type  $\text{M}_2\text{X}_2$  not being represented by the halides of this element.

The type  $\text{XR}_4$  represents the halanhydrides of the orthoacids  $\text{X}(\text{OH})_4$ , corresponding with the dioxides; these, however, do not exist, and the halides of this type when decomposed by water yield the  $\text{OX}(\text{OH})_2$  acids, derived from the  $\text{X}(\text{OH})_4$  type by dehydration; for instance,



The tetrachlorides of selenium and tellurium, however, first yield the oxychlorides,  $\text{SeOCl}_2$  and  $\text{TeOCl}_2$ , which are finally decomposed, giving the oxyacids.

There are no oxyacids corresponding to any lower type of halide than  $\text{XR}_4$ . The lower halides are, however, decomposed by water, with the formation of oxyacids of the type  $\text{OX}(\text{OH})_2$  and separation of the elements; for example,



#### THE OXIDES

Oxides of a number of types are known:

XO	—	SeO(?)	TeO
$\text{X}_2\text{O}_3$	$\text{S}_2\text{O}_3$	$(\text{SeSO}_3, \text{TeSO}_3, \text{TeSeO}_3)$	
$\text{XO}_2$	$\text{SO}_2$	$\text{SeO}_2$	$\text{TeO}_2$
$\text{XO}_3$	$\text{SO}_3$	—	$\text{TeO}_3$
$\text{X}_2\text{O}_7$	$\text{S}_2\text{O}_7$	—	—

Of these the type XO is unimportant, the existence of SeO being doubtful, and TeO giving rise to no salts. The acidic oxides  $\text{XO}_2$  and  $\text{XO}_3$ , in the latter of which the maximum oxygen valency is displayed, are the most characteristic, and correspond with the oxyacids  $\text{OX}(\text{OH})_2$  and  $\text{O}_2\text{X}(\text{OH})_2$ , the more completely hydroxylated types  $\text{X}(\text{OH})_4$ ,  $\text{OX}(\text{OH})_4$ , and  $\text{X}(\text{OH})_6$  being unknown, except in the form of certain basic sulphates,

*e.g.*  $\text{OS}(\text{O}_2\text{Pb})_2$  and  $\text{S}(\text{O}_2\text{Hg}'')_3$ . Tellurium dioxide has also feebly basic properties, yielding unstable salts such as  $\text{Te}(\text{SO}_4)_2$ ; this is in harmony with the position of tellurium in the group.

It will be more convenient to deal with oxides of the type  $\text{X}_2\text{O}_3$  later.

#### OXIDES $\text{XO}_2$ AND DERIVED ACIDS

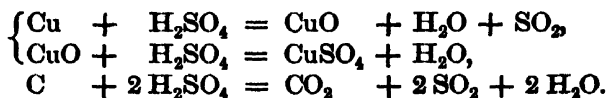
The oxides,  $\text{XO}_2$ , known for each element, result from the direct union of the elements with oxygen. While sulphur dioxide is a gas easily condensible to a liquid, boiling at  $-8^\circ$ , selenium dioxide is a crystalline solid subliming at about  $300^\circ$ , and tellurium dioxide also a solid easily melting to a yellowish liquid, which boils without decomposition.

It will be remembered in the case of the fifth group that phosphorus forms phosphoric oxide, and arsenic arsenious oxide, on combustion. The analogous elements of the sixth group unite spontaneously with a less atomic proportion of oxygen than phosphorus, being rather analogous to arsenic in power of oxidation; and those of the seventh group are non-combustible, bromine, indeed, forming no oxide. Sulphur approximates to phosphorus in forming a little of the higher oxide by direct combustion. When selenium and tellurium are warmed with nitric acid they yield selenious and tellurous acids,  $\text{H}_2\text{SeO}_3$  and  $\text{H}_2\text{TeO}_3$ , respectively, each of which exists in the solid state. Associated with this physical property of the acids is that of easy dehydration, for these two acids readily yield their anhydrides;  $\text{TeO}_2$ , indeed, separating from the nitric-acid solution of the element.

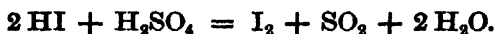
This tendency towards dehydration is manifested by acids derived from metalloids or weak metals, whose oxides are feeble anhydrides. Sometimes poly-acids or their salts exist, representing intermediate products of dehydration, as in the case of chromic, molybdic, and tungstic acids. Oxides of non-metals which are powerful anhydrides, *e.g.*  $\text{N}_2\text{O}_5$ ,  $\text{P}_2\text{O}_5$ ,  $\text{SO}_3$ , combine with, and retain, water with avidity, and the acids are generally liquids or solids of low melting-point.

The dioxides,  $\text{XO}_2$ , may also be obtained by reduction of the  $\text{XO}_3$  oxides or the corresponding  $\text{H}_2\text{XO}_4$  acids; as, for

example, in the well-known method of preparation of sulphur dioxide from sulphuric acid by warming the concentrated acid with metals (such as Cu, Ag, Hg, Zn), or with carbon or sulphur. In these reactions the sulphuric acid may be regarded as acting as an oxidizing agent; thus:—



Similarly, concentrated sulphuric acid oxidizes hydriodic acid, and less readily also hydrobromic acid:



Loss of oxygen may occur even by simple heating; thus selenic acid gives water, oxygen, and  $\text{SeO}_2$ , whilst  $\text{SO}_3$  and  $\text{TeO}_3$  are both decomposed into the dioxides and oxygen when heated strongly.

The acids,  $\text{H}_2\text{XO}_3$ , corresponding with the  $\text{XO}_2$  oxides, represent the first and only meta-derivatives of the hypothetical type,  $\text{X(OH)}_4$ ; they are sulphurous, selenious, and telluric acids. Sulphur and selenium dioxides both dissolve in water, yielding the acids, but tellurium dioxide is only very slightly soluble in water and alkalis, and its aqueous solution does not redden blue litmus. Whilst selenious and telluric acids can both be isolated in the pure state, sulphurous acid belongs to the category of easily decomposable acids (such as carbonic, silicic, nitrous), readily giving sulphur dioxide when the aqueous solution is heated, although solid crystallo-hydrates separate from saturated aqueous solutions at low temperatures. The instability of sulphurous acid may be attributed partly to the gaseous nature of sulphur dioxide, but is also due to its feebly anhydride character.

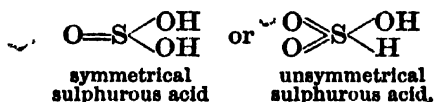
It is remarkable that whilst sulphurous acid acts as a reducing agent, selenious acid is itself easily reduced, for example by sulphur dioxide or organic matter. Sulphurous acid is, however, reduced by a powerful reducing agent such as phosphorous acid, sulphur being precipitated. The affinity of

selenium for oxygen appears to be less than the affinities of its allied elements, as is further shown by the non-existence of an oxide,  $\text{SeO}_3$ .

These acids are dibasic, giving rise to normal salts, such as in the case of sulphur,  $\text{Na}_2\text{SO}_3$ ,  $\text{K}_2\text{SO}_3$ ,  $\text{CaSO}_3$ , and to acid salts, such as the bisulphites,  $\text{NaHSO}_3$  and  $\text{KHSO}_3$ .<sup>1</sup>

### SULPHUROUS ACID AND SULPHITES

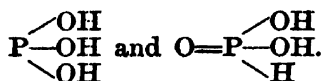
In considering the structure of sulphurous acid and its salts two possibilities are presented; the acid may be formulated:



the metallic salts possessing corresponding constitutions; just as with nitrous acid there are the two possible structures:



and with phosphorous acid,



It may be pointed out that such dual structures are theoretically possible in all cases where the nuclear atom is incompletely oxidized; and it is to be supposed that the stability of the unsymmetrical form will depend on the oxidizability of this atom.

†The oxychloride,  $\text{SOCl}_2$ , thionyl chloride, a colourless liquid boiling at  $78^\circ$ , which may be obtained by the action of phosphorus pentachloride on sodium sulphite,



or by the reaction



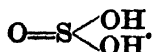
<sup>1</sup> In the solid state these salts exist as  $\text{M}'_2\text{S}_2\text{O}_6$ , resulting from  $2\text{M}'\text{HSO}_3$  by loss of water. They are often known as metabisulphites, but are correctly designated pyrosulphites.

corresponds with  $\text{H}_2\text{SO}_3$ , into which it is converted by water, and of which, therefore, it is the chloride:

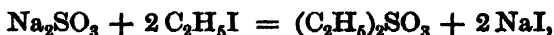


With alcohol it yields, similarly, the ethyl ester  $(\text{C}_2\text{H}_5)_2\text{SO}_3$ .

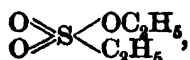
Now the structure of thionyl chloride must almost certainly be  $\text{O}=\text{S} \begin{smallmatrix} \text{Cl} \\ \diagup \\ \text{Cl} \end{smallmatrix}$ , and that of the ethyl salt is therefore  $\text{O}=\text{S} \begin{smallmatrix} \text{OC}_2\text{H}_5 \\ \diagup \\ \text{OC}_2\text{H}_5 \end{smallmatrix}$ ; thus it is symmetrical ethyl sulphite, and is a liquid boiling at  $161^\circ$ . Similarly, aqueous sulphurous acid, which may be obtained by causing thionyl chloride to react with water, must possess, at least at the moment of its formation, the formula



Ethyl sulphite, when treated with sodium hydroxide, is hydrolysed, yielding sodium sulphite and alcohol; and when sodium sulphite is digested with ethyl iodide, a product is obtained according to the reaction



which, however, is not identical with the ethyl sulphite described above, since it boils at  $207^\circ$ . Moreover, when hydrolysed, this product yields sodium ethylsulphonate,  $\text{NaC}_2\text{H}_5\text{SO}_3$ , a salt of ethylsulphonic acid. And since ethylsulphonic acid results from the oxidation of mercaptan,  $\text{C}_2\text{H}_5\text{SH}$ , in which ethyl is undoubtedly attached to sulphur, it follows that the above isomer, boiling at  $207^\circ$ , is ethyl ethylsulphonate:



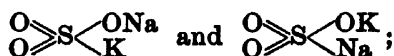
and is derived from unsymmetrical sulphurous acid:



Sodium sulphite, which gives rise to this derivative, is therefore in all probability

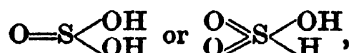


This unsymmetrical formula suggests the existence of two isomeric sodium potassium sulphites,

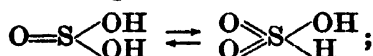


and it was formerly supposed that such salts are formed respectively when sodium hydrogen sulphite is neutralised with potassium carbonate, and when potassium hydrogen sulphite is neutralised with sodium carbonate. According to Godby,<sup>1</sup> however, there is no evidence of the existence of these isomerides, and Arbusoff<sup>2</sup> has found that methyl iodide always gives the same product,  $\text{CH}_3 \cdot \text{SO}_2 \cdot \text{OK}$ , with  $\text{NaKSO}_3$ , however the latter is prepared.

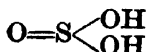
These considerations, however, leave the constitution of sulphurous acid itself unsettled; so that the acid may be either



or a mixture of these in equilibrium,



for, on conversion into a salt, the form



might yield the form



by molecular rearrangement.

Selenious and telluric acids do not present phenomena analogous to those described above in the case of sulphurous acid.

Ethyl selenite,  $\text{O}=\text{Se} \begin{smallmatrix} \text{OC}_2\text{H}_5 \\ \text{OC}_2\text{H}_5 \end{smallmatrix}$ , is obtained both by the action of sodium ethoxide on selenosyl chloride,  $\text{O}=\text{Se} \begin{smallmatrix} \text{Cl} \\ \text{Cl} \end{smallmatrix}$ , and of ethyl iodide on silver selenite. Selenious acid appears, therefore, to be symmetrical even in the form of its inorganic

<sup>1</sup> *Chem. Soc. Proc.*, 1907, 23, 241.

<sup>2</sup> *J. Russ. Phys. Chem. Soc.*, 1909, 41, 447.

salts, and the same is probably true of tellurous acid; this difference may be attributed to the inferior oxidizability of selenium and tellurium as compared with sulphur.

Pyroselenites and pyrotellurites, analogous to pyrosulphites, are unknown.

#### OXIDES $XO_3$ AND DERIVED ACIDS

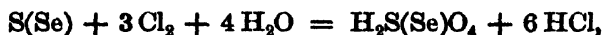
Of the  $XO_3$  oxides,  $SO_3$  and  $TeO_3$  alone are known, and are produced by oxidation of the lower oxides.

Direct union of sulphur dioxide and oxygen occurs under the catalytic influence of finely-divided platinum at a moderate temperature; a reaction which has long been known, but has only recently been so perfected as to afford a commercial source of the oxide, and therefore, also, of sulphuric acid.<sup>1</sup>

The acids  $H_2XO_4$  are represented by sulphuric, selenic, and telluric acids. Of the anhydrides,  $SO_3$  and  $TeO_3$ ,  $SO_3$  alone unites directly with water,  $TeO_3$  being unaltered by that substance (*cf.*  $TeO_2$ ).

Each of the acids of this type is produced by the oxidation either of the element or of the lower acid; as, for instance, in the case of sulphurous acid by the catalytic action of the lower oxides of nitrogen in the well-known sulphuric acid chamber process.

Sulphur and selenium are oxidized by chlorine in the presence of water; thus:—



and potassium<sup>2</sup>tellurate results from the action of chlorine on the tellurite in alkaline solution,



free telluric acid being obtained from the potassium salt by conversion, by means of barium chloride, into the sparingly

<sup>1</sup> See R. Knietzsch, *Berichte* (1901), xxxiv, 4069. One of the chief difficulties encountered in the process was the gradual decrease in activity of the platinum. This was eventually found to be caused by arsenic, which arrests the catalytic action; and it was only when the gases were free from this substance that the process could be made continuous.



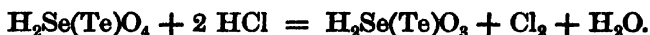
soluble barium tellurate, which is then decomposed by the requisite amount of sulphuric acid. Each of these acids may be obtained in the pure state.

**Sulphuric acid** melts at  $10\cdot5^\circ$ ; **selenic acid** at  $58^\circ$ ; **telluric acid** does not melt.

Sulphuric and selenic acids readily unite with water, forming crystallohydrates; telluric acid forms a definite compound,  $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$ , which gives  $\text{H}_2\text{TeO}_4$  at  $160^\circ$ .

The three acids differ in important respects, and their differences serve further to illustrate the periodic variation of properties. Thus sulphuric acid can be distilled, and only breaks up into sulphur dioxide, water, and oxygen at a red heat; but selenic acid begins to decompose into selenium dioxide, oxygen, and water at about  $280^\circ$ , and telluric acid at a low red heat easily gives the anhydride, which further decomposes into the dioxide and oxygen.

Owing to the greater ease with which they lose oxygen, selenic and telluric acids are more powerful oxidizing agents than sulphuric acid. For example, the latter acid does not act upon hydrochloric acid, but selenic and telluric acids both yield, with strong hydrochloric acid, the lower acids and chlorine; thus:—



Thus  $\text{BaSeO}_4$  differs from  $\text{BaSO}_4$  by dissolving in strong hydrochloric acid. As dibasic acids, each of these acids gives rise to both normal and acid salts of the types  $\text{M}'_2\text{XO}_4$  and  $\text{M}'\text{HXO}_4$ . On careful heating, the acid or hydrogen sulphates of the alkali metals produce pyrosulphates by loss of water; *e.g.* :—

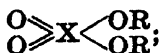


Telluric acid further forms acid salts, such as  $\text{K}_2\text{TeO}_4$ ,  $\text{TeO}_3$ ,  $4\text{H}_2\text{O}$ , and  $\text{K}_2\text{TeO}_4 \cdot 3\text{TeO}_3 \cdot 4\text{H}_2\text{O}$ , a behaviour recalling that of chromic acid in producing the di- and trichromates. Tellurium shows a further resemblance to the members of Group VI A by forming complex phospho- and arsenitelluric acids.

Selenates are isomorphous with sulphates, and form alums,

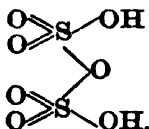
but tellurates are more closely allied to chromates, with which they are sometimes isomorphous.

There can be little doubt that the structure of these acids and their salts is correctly represented by the graphic formula



no isomerism of mixed sulphates (such as  $\text{KNaSO}_4$ ) is known, and in the alkyl sulphates (such as  $(\text{CH}_3)_2\text{SO}_4$ ) there is no reason to suppose that either of the alkyl groups is not attached to oxygen.

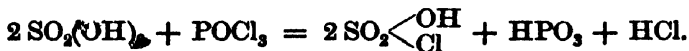
Pyro- or disulphuric acid<sup>1</sup> will therefore be formulated,



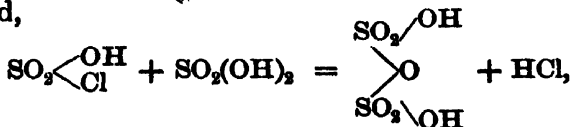
Each of these acids further corresponds with an oxychloride,  $\text{XO}_2\text{Cl}_2$ , sulphur also forming the half-oxychloride,  $\text{SO}_2\text{Cl}\text{OH}$ ,

chlorosulphonic acid, and  $\begin{array}{c} \text{O}_2\text{S} \quad \text{Cl} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$ , disulphuryl chloride, corresponding with disulphuric acid.

Chlorosulphonic acid is prepared by the direct union of sulphuric anhydride and dry hydrogen chloride, or by the action of phosphorus oxychloride on sulphuric acid,

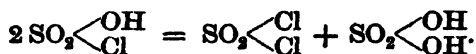


It is a colourless liquid boiling at  $152^\circ$ , and it is easily decomposed by water, giving sulphuric and hydrochloric acids; with strong sulphuric acid, disulphuric and hydrochloric acids are formed,



<sup>1</sup> This acid is crystalline, melting at  $35^\circ$ ; its solution in  $\text{H}_2\text{SO}_4$  is known as Nordhausen or fuming sulphuric acid.

and on heating alone at  $180^{\circ}$  it is resolved into sulphuryl chloride and sulphuric acid,



† Sulphuryl chloride,  $\text{SO}_2\text{Cl}_2$ , is also prepared, however, by the direct union of sulphur dioxide and chlorine, a reaction which occurs slowly in strong light, but which is readily brought about by allowing the gases to come into contact with camphor, the rôle of that substance in the reaction being unknown. It is a colourless liquid boiling at  $69^{\circ}$ , and like chlorosulphonic acid is converted by water into sulphuric and hydrochloric acids; it is the true chloride of sulphuric acid.

#### OTHER ACIDS

In addition to the characteristic types of sulphurous and sulphuric, sulphur gives rise to a considerable number of other oxyacids, which are here enumerated:—

- Hyposulphurous acid  $\text{H}_2\text{S}_2\text{O}_4$
- ✓Thiosulphuric acid  $\text{H}_2\text{S}_2\text{O}_3$
- Dithionic (hyposulphuric) acid  $\text{H}_2\text{S}_2\text{O}_6$
- Trithionic acid  $\text{H}_2\text{S}_3\text{O}_6$
- Tetrathionic acid  $\text{H}_2\text{S}_4\text{O}_6$
- Pentathionic acid  $\text{H}_2\text{S}_5\text{O}_6$
- [Hexathionic acid  $\text{H}_2\text{S}_6\text{O}_6$ ].<sup>1</sup>

Corresponding with thiosulphuric acid there is also selenosulphuric acid,  $\text{H}_2\text{SeSO}_3$ , and with trithionic acid, selenotrithionic acid,  $\text{H}_2\text{SeS}_2\text{O}_6$ , in both of which selenium may be regarded as taking the place of sulphur.

Persulphuric acid (perdisulphuric acid),  $\text{H}_2\text{S}_2^4\text{O}_8$ , and “Caro’s acid”, or permonosulphuric acid,  $\text{H}_2\text{SO}_5$ , along with the anhydride  $\text{S}_2\text{O}_7$ , belong to the class of “per” compounds, and will be dealt with in a separate section.

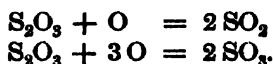
✓**Hyposulphurous acid.**—The zinc salt of this acid is produced when sulphurous-acid solution is treated with zinc, the metal dissolving without evolution of hydrogen. When sodium-hydrogen-sulphite solution is used, sodium hypo-

<sup>1</sup> Existence doubtful.

sulphite results, and may be obtained crystalline,  $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ . Free hyposulphurous acid has never been obtained in the pure state. The hyposulphites are powerful reducing agents, bleaching organic matter, and precipitating silver and mercury from their salts. On account of the former action they receive commercial application. They readily absorb oxygen, yielding sulphites.

The formula  $\text{H}_2\text{SO}_2$  was attributed to hyposulphurous acid by the discoverer, Schützenberger. This would correspond to an anhydride,  $\text{SO}$ , whilst  $\text{H}_2\text{S}_2\text{O}_4$  corresponds to  $\text{S}_2\text{O}_3$ . The formula  $\text{H}_2\text{S}_2\text{O}_4$  was thus proved by Bernthsen:—

Ammoniacal copper sulphate oxidizes hyposulphite to sulphite, iodine oxidizes to sulphate. It was found that for every two atoms of sulphur as hyposulphite, one atom of oxygen is required to oxidize to sulphite, and three to sulphate; thus:—



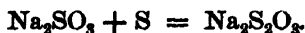
Therefore hyposulphite corresponds to the anhydride  $\text{S}_2\text{O}_3$ , rather than to  $\text{SO}$ .<sup>1</sup>

✂ **Sulphur sesquioxide**,  $\text{S}_2\text{O}_3$ , is obtained as a blue-green crystalline mass by the direct union of sulphur and sulphur trioxide. A beautiful indigo-blue colour is formed when Nordhausen acid is poured on flowers of sulphur. The sesquioxide does not give hyposulphurous acid with water, but forms sulphur, sulphurous and sulphuric acids; since, however, a solution of hyposulphurous acid undergoes a similar change, it cannot be definitely asserted that the oxide is not the anhydride of the acid.

✂ **Thiosulphuric acid**,  $\text{H}_2\text{S}_2\text{O}_3$ , still commonly called hyposulphurous acid, is not known in the pure state, although dilute solutions are formed by the action of flowers of sulphur on sulphurous acid at about  $80^\circ$ . The salts, however, are

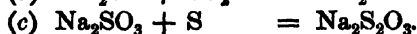
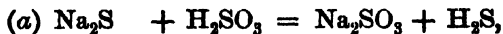
<sup>1</sup> According to Bucherer and Schwalbe (*Zeit. Angew. Chem.*, 1904, xvii, 1447), sodium hyposulphite is an acid salt,  $\text{Na}_2\text{H}_2\text{S}_2\text{O}_3$  or  $\text{O} \begin{array}{c} \text{S(OH)ONa} \\ | \\ \text{S(OH)ONa} \end{array}$ , to which a normal salt  $\text{Na}_2\text{S}_2\text{O}_3$  would correspond.

more stable. They are produced by the action of sulphur on the sulphites, thus:—

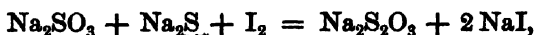


Selenium similarly dissolves in  $\text{Na}_2\text{SO}_3$  forming  $\text{Na}_2\text{SeSO}_3$ .

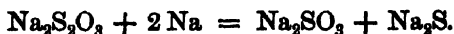
The formation of thiosulphate on a large scale, by leading sulphur dioxide into alkali or alkaline-earth sulphide solutions, depends on the same reaction, as the following equations show:—



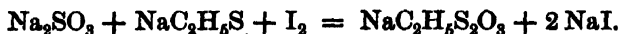
When iodine acts on a mixture of alkali sulphite and sulphide, a thiosulphate results:



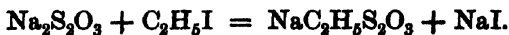
and sodium thiosulphate is reduced by sodium amalgam, reproducing its generators,



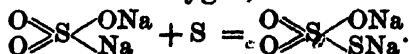
If sodium ethyl sulphide is substituted for sodium sulphide in the above reaction, sodium ethyl thiosulphate (Bunte's salt) results, thus:



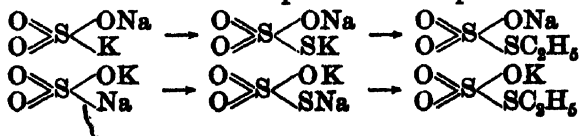
The same salt is formed when ethyl iodide reacts with sodium thiosulphate:



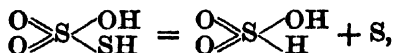
There is no doubt that the thiosulphates must be considered as sulphates in which one atom of oxygen has been replaced by one atom of sulphur, the addition of sulphur to a sulphite resembling the addition of oxygen,



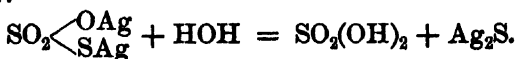
The isomeric sodium potassium thiosulphates, supposed to be derived from isomeric sodium potassium sulphites thus:



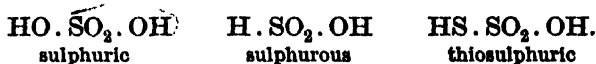
probably do not exist. Thiosulphuric acid readily parts with I sulphur, forming sulphurous acid,



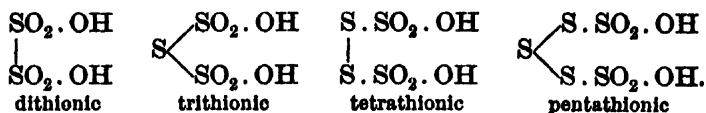
and the relationship of the acid to sulphuric acid is illustrated II by the hydrolysis by water of such salts as the thiosulphates of silver and cobalt with the formation of sulphides and sulphuric acid:



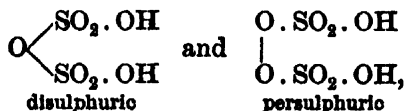
Both sulphurous and thiosulphuric acids contain the group— $\text{SO}_2 \cdot \text{OH}$ , which is characteristic of sulphonic acids, such as benzene sulphonic acid,  $\text{C}_6\text{H}_5 \cdot \text{SO}_2 \cdot \text{OH}$ . The relationship to sulphuric acid is made clear by the formulæ:



Similarly, the thionic acids may be regarded as sulphonic acids obtained either by direct union of sulphonic groups or their linkage through a sulphur atom or atoms. Their structures are indicated by the following formulæ:—

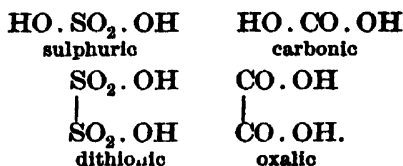


The oxygen analogues of tri- and tetrathionic acids are:

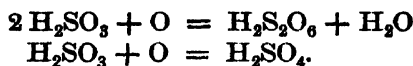


and just as sulphuric, disulphuric, and persulphuric acids may be regarded as derived from water and hydrogen peroxide by the replacement of hydrogen by the sulphonic group, so the thionic acids may be viewed similarly as derivatives of sulphuretted hydrogen and the persulphides of hydrogen.

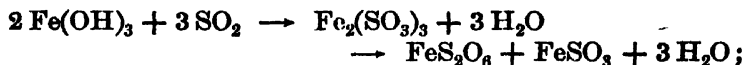
✓ **Dithionic acid** bears the same relationship to sulphuric acid as oxalic bears to carbonic acid:



It is formed by the partial oxidation of sulphurous acid, complete oxidation resulting in the formation of sulphuric acid, thus:



When ferric hydroxide reacts with sulphur dioxide in presence of water, ferric sulphite, which is first formed, undergoes self-oxidation and reduction to ferrous dithionate and sulphite, thus:



but dithionate is usually prepared by passing sulphur dioxide through water in which manganese dioxide is suspended:



From the manganese salt a solution of the acid or its alkali salts can be obtained. The acid is not known in the pure state.

Sodium dithionate is reduced in aqueous solution by sodium amalgam, sulphite being regenerated:

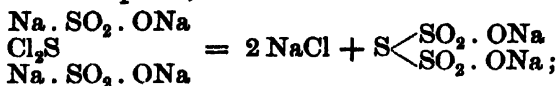


✗ **Trithionic acid**,  $\text{H}_2\text{S}_3\text{O}_6$ . Potassium trithionate is formed when sulphur dioxide reacts with a solution of potassium thiosulphate:

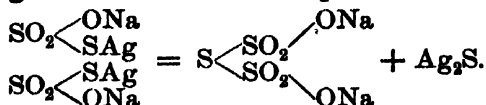


The free acid is unstable.

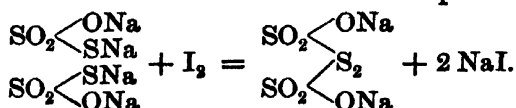
Trithionate may also be obtained by the action of sulphur dichloride on a sulphite, thus:



and by heating sodium silver thiosulphate with water:



✓ **Tetrathionic acid.**—Sodium tetrathionate is formed in the well-known reaction between sodium thiosulphate and iodine:



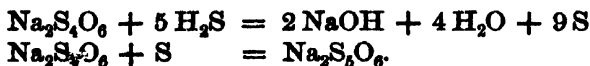
Ferric chloride reacts in an analogous way with thiosulphate:



The reaction is reversed by sodium amalgam, thiosulphate being regenerated.

Tetrathionic acid may be obtained in solution by decomposing its barium salt with dilute sulphuric acid.

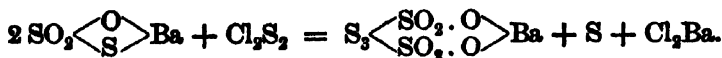
✓ **Pentathionic acid.**—A tetrathionate can combine with nascent sulphur to form pentathionate, and the following reactions take place when hydrogen sulphide is passed into a solution of sodium tetrathionate:—



Pentathionate is also formed together with trithionate by the spontaneous decomposition of a solution of tetrathionate,



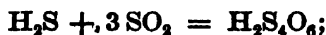
and also by the action of sulphur chloride on barium thiosulphate,



Salts of this acid are, however, generally obtained from Wack-

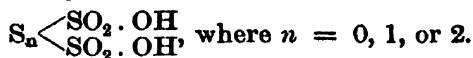


enroder's solution, the liquid formed by passing hydrogen sulphide into strong sulphurous-acid solution at  $0^{\circ}$ . Although the final products of the interaction of sulphuretted hydrogen and sulphur dioxide are sulphur and water, that result is preceded by the formation of polythionic acids, the first of which is probably tetrathionic,



thence by secondary reactions tri- and pentathionic acids result; and from the solution the alkali salt of the latter acid can be isolated by a lengthy process.

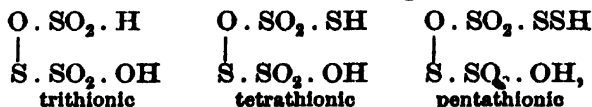
**Constitution of the thionic acids.**—The formation of di-, tri-, and tetrathionic acids by the reactions of condensation which have been studied above, and the reversal of these reactions by sodium amalgam, are explained by representing the acids by the general formula:



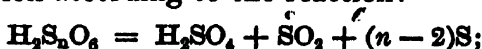
Pentathionic acid may be supposed to be similarly constituted, in which case  $n = 3$ .

The reactions with iodine and sodium amalgam were studied by Spring, and the above conclusions as regards constitution have been adopted by Mendeléeff.

Debus, however, who investigated the thionic acids, attributed to the latter three the following formulæ:



The following comparative reactions of thionic acids may be mentioned. Aqueous solutions of all the acids decompose on concentration according to the reaction:

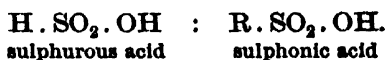


the solid salts decompose in analogous fashion on heating. Dithionic acid, since its molecule contains but two atoms of sulphur, yields no sulphur on decomposition. Tetrathionic is the most stable of these acids. The barium salts are all

soluble in water, but mercurous nitrate gives with trithionate solutions a black precipitate and with tetra- and pentathionates yellow precipitates. On warming with copper-sulphate solution, trithionate gives a black precipitate. Easy decomposition by bases is characteristic of pentathionates.

Certain types of organic compounds containing sulphur may here be mentioned.

**Sulphonic acids**, as previously observed, are derivatives of unsymmetrical sulphurous acid:



**Sulphinic acids** are related to the unsymmetrical form of the hypothetical  $\text{H}_2\text{SO}_2$ :



**Sulphoxides** and **sulphones** are formed by the oxidation of sulphides; thus:—



**Sulphonium bases**,  $\text{SR}_3\text{OH}$ , and their salts, such as triethyl sulphonium iodide,  $(\text{C}_2\text{H}_5)_3\text{SI}$ , are related to  $\text{SH}_2$ , as ammonium hydroxide and its salts to  $\text{NH}_3$ . The alkyl sulphonium halides are formed by the combination of alkyl sulphides and alkyl halides; thus—



which is analogous to the reaction:



Asymmetric sulphonium salts of the type  $\text{R}_1\text{R}_2\text{R}_3\text{SA}$  have been resolved into optically active components by Pope and Peachey,<sup>1</sup> and by Smiles,<sup>2</sup> it thus being shown that the disposition of the valencies of the tetravalent sulphur atom is analogous to that obtaining with carbon.

<sup>1</sup> *Chem. Soc. Trans.* lxxvii (1900), 1072.

<sup>2</sup> *Chem. Soc. Trans.* lxxvii (1900), 1174.

## APPENDIX TO SUB-GROUP VI B

*The Acidic Derivatives of Hydrogen Peroxide*

As was mentioned in the chapter on oxides, the peroxides may be divided into two classes: the polyoxides, containing several doubly-linked oxygen atoms, and the superoxides, which contain oxygen chains, such as:



and



There is at present no sufficient ground for assigning to hydrogen peroxide<sup>2</sup> a constitution other than  $\text{H}-\text{O}-\text{O}-\text{H}$ , such as the structure  $\begin{array}{c} \text{H} \\ \text{H} \end{array} > \text{O}=\text{O}$  advocated by Bach; and the former formula will accordingly be employed here.

Of superoxides of acidic character that of sulphur,  $\text{S}_2\text{O}_7$ , is the chief example. It is formed by the union of sulphur dioxide and oxygen under the influence of the silent electric discharge, and is a volatile liquid, solidifying at  $0^\circ$  and changing gradually at atmospheric temperature, though rapidly on heating, to the trioxide and oxygen. With water it yields sulphuric acid and oxygen.

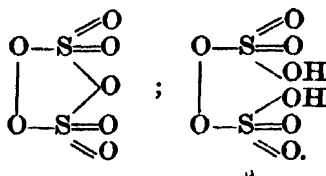
<sup>1</sup> Although sulphur forms with hydrogen higher sulphides, of which  $\text{H}_2\text{S}_8$  is the most stable, the evidence for the existence of analogous higher oxides of hydrogen is not so far conclusive.

Sodium polysulphides,  $\text{Na}_2\text{S}_3$  and  $\text{Na}_2\text{S}_8$ , have been obtained crystalline. When a solution of a polysulphide is poured into excess of concentrated hydrochloric acid, oily drops separate, having a composition which lies between  $\text{H}_2\text{S}_3$  and  $\text{H}_2\text{S}_8$ . When acid is poured into a solution of a polysulphide, sulphur is precipitated, and  $\text{H}_2\text{S}$  evolved.

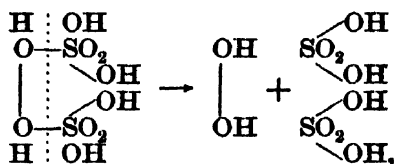
<sup>2</sup> Pure hydrogen peroxide, best obtained by decomposing sodium peroxide with dilute sulphuric acid, extracting with ether, or evaporating *in vacuo* and distilling under reduced pressure, is a syrupy liquid of sp. gr. 1.46, boiling at  $69^\circ$  under 28 m.m. pressure, and solidifying at  $-2^\circ$ . It is strongly acid in reaction, and decomposes sodium carbonate; superoxides, such as  $\text{Na}_2\text{O}_2$ ,  $\text{BaO}_2$ , and  $\text{HgO}_2$ , formed by its action on mercury, are its salts.

Finely divided solid matter, especially powdered and colloidal metals, promote the catalytic decomposition of an aqueous solution of  $\text{H}_2\text{O}_2$ .  $\text{H}_2\text{O}_2$  is less stable in alkaline than in acid solution, and oxidises various metallic hydroxides, sulphides, and salts under conditions favourable to the stability of the oxidation products. With oxidizing substances such as ozone, permanganic acid, and silver oxide there is mutual reduction with evolution of oxygen.

The structures of this oxide, and of perdisulphuric acid, of which it is the anhydride, are thus represented:

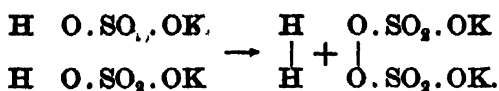


Water first converts the anhydride into the acid; and the subsequent production of sulphuric acid and oxygen depends firstly on the slow hydrolysis of perdisulphuric acid to sulphuric acid and hydrogen peroxide (Baeyer):



and secondly, on the decomposition of  $\text{H}_2\text{O}_2$  into water and oxygen.

Although perdisulphuric acid is not known in the pure state, a dilute solution may be prepared, and several pure salts are obtainable. Potassium perdisulphate, or persulphate as it is usually called, results, as Marshall<sup>1</sup> has shown, from the electrolytic oxidation of a solution of potassium hydrogen sulphate. The principle of the reaction is the same whether sulphuric acid or potassium hydrogen sulphate is electrolysed, and depends upon the existence of  $\text{HSO}_4$  or  $\text{KSO}_4$  ions in the liquid, which, becoming concentrated at the anode, and giving up their charges, unite in pairs to form  $\text{H}_2\text{S}_2\text{O}_8$  and  $\text{K}_2\text{S}_2\text{O}_8$  respectively. In the case of the potassium salt, crystals are obtained at the anode; thus:—



The salt has therefore the formula  $\text{K}_2\text{S}_2\text{O}_8$  and not  $\text{KSO}_4$ . It is rather sparingly soluble, all the persulphates being soluble

<sup>1</sup> *Chem. Soc. Trans.* lix (1891), 771.

in water; and, as might be expected, it is a powerful oxidizing agent, oxidizing ferrous salts, liberating chlorine from hydrochloric acid, and iodine from potassium iodide, and precipitating higher oxides from solutions of silver, copper, manganese, cobalt, and nickel salts. Pure persulphuric acid does not readily reduce permanganate, thus differing from hydrogen peroxide.

When heated alone the potassium salt gives sulphate, sulphur trioxide, and oxygen,

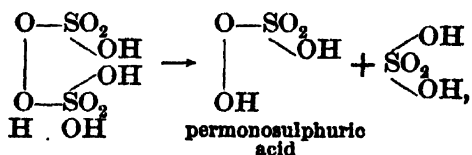


and on boiling a solution of persulphate the following change takes place:—



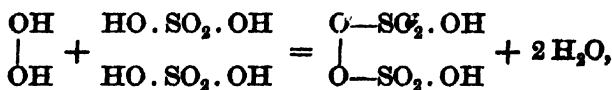
This reaction furnishes a ready means of estimating the salt by the titration of the acid produced.

On mixing dry potassium persulphate with concentrated sulphuric acid containing one molecular proportion of water at low temperature, perdisulphuric acid is liberated, and fairly rapidly hydrolysed by water, yielding the so-called **Caro's acid**, or **permonosulphuric acid**,  $\text{H}_2\text{SO}_5$ , and  $\text{H}_2\text{SO}_4$ ; thus:—

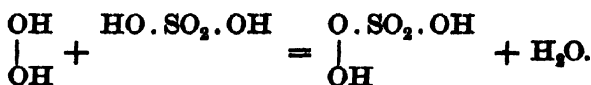


so that on dilution (with ice) a solution is obtained from which the sulphuric acid may be removed by precipitation with barium phosphate.

Both peracids may also be made by the direct sulphonation of hydrogen peroxide by the action of sulphuric acid on its cold solution; thus:—



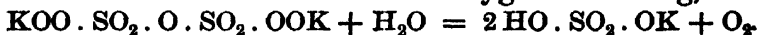
and



Permonosulphuric acid liberates iodine rapidly from potassium iodide, whilst perdisulphuric acid does so more slowly, so that the proportions of the two acids in a mixture may be approximately determined. Barium hydroxide causes rapid hydrolysis to sulphuric acid and hydrogen peroxide, but sodium hydroxide acts in this manner less readily.

The formula,  $\text{H}_2\text{SO}_5$ , for the permonoacid, which has been assumed in the preceding paragraph, is based upon a determination, by von Baeyer and Villiger, of the ratio of active oxygen to  $\text{SO}_3$ .

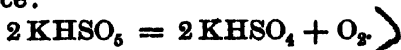
Armstrong and Lowry,<sup>1</sup> however, consider that Caro's acid is anhydropermonosulphuric acid,  $\text{H}_2\text{S}_2\text{O}_9$ , a dibasic acid having the constitution  $\text{HOO} \cdot \text{SO}_2 \cdot \text{O} \cdot \text{SO}_2 \cdot \text{OOH}$ , because a neutral salt solution becomes acid and loses oxygen on boiling, thus:



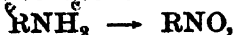
But Slater Price<sup>2</sup> has shown by the loss of weight the potassium salt, mixed with known amounts of other salts, undergoes on ignition, that the formula  $\text{H}_2\text{SO}_5$  is more probable than  $\text{H}_2\text{S}_2\text{O}_9$ ; and this conclusion has been confirmed by Ahrle,<sup>3</sup> who has prepared the free acid nearly pure by adding sulphuric anhydride to anhydrous hydrogen peroxide.

It may therefore be concluded that Caro's acid, or permonosulphuric acid, should be represented by the formula  $\text{H}_2\text{SO}_5$ ; but that it is monobasic, its potassium salt being  $\text{KO} \cdot \text{SO}_2 \cdot \text{OOH}$ , since the remaining hydrogen atom, as part of  $\text{H}_2\text{O}_2$ , will not be appreciably ionised in solution.

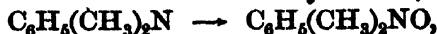
Then on boiling the potassium salt solution the following change takes place:



Permonosulphuric acid possesses specific oxidizing powers, of value in the study of organic compounds. For instance, primary aromatic amines are oxidized to nitrosocompounds,



tertiary fatty-aromatic amines to oxyamines,

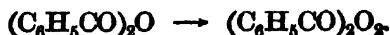


<sup>1</sup> *Roy. Soc. Proc.* lxx. (1902), 94.

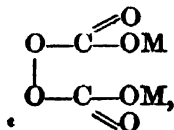
<sup>2</sup> *Chem. Soc. Trans.*, 1906, 89, 58.

<sup>3</sup> *Zett. Angew. Chem.*, 1909, 22, 1713.

and anhydrides of acids to peranhydrides, *e.g.* :—



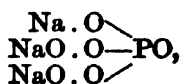
**Percarbonates**,  $\text{M}'_2\text{C}_2\text{O}_6$ , of the structure



are also obtainable by the electrolytic method, and form convenient oxidizing agents, affording alkaline hydrogen peroxide solutions.

On treatment of **chromic, molybdic, tungstic, and uranic acids** or their salts with hydrogen peroxide, **peracids** are produced. These appear to correspond to a combination of the tetroxide  $\text{XO}_4$  with hydrogen peroxide or its equivalent. **Sodium peruranate**, for instance, is  $\text{Na}_4\text{UO}_8 \cdot 8\text{H}_2\text{O}$  ( $\text{Na}_4\text{UO}_8 = 2\text{Na}_2\text{O}_2 \cdot \text{UO}_4$ ). The well-known blue **perchromic acid**, obtained by the action of hydrogen peroxide on chromic-acid solution, is not derived from  $\text{Cr}_2\text{O}_7$ , as was formerly thought, but from  $\text{CrO}_4$ . The compound  $\text{KCrO}_5 \cdot \text{H}_2\text{O}_2$  ( $2\text{KCrO}_5 = \text{K}_2\text{O}_2 \cdot 2\text{CrO}_4$ ) has been obtained as a violet crystalline powder.

Some other acids, such as boric, yield persalts on treatment with alkali peroxide, for instance the salts  $\text{MBO}_3$  (probably  $\text{MO} \cdot \text{O} - \text{B} = \text{O}$ ); phosphates also form compounds with metallic peroxides, such as:



although phosphoric acid and hydrogen peroxide do not yield a corresponding perphosphoric acid.

P. Melikoff summarizes the formation of peracids and salts as follows:—By the action of hydrogen peroxide on salts there may be formed:

- Compounds of peracids with metallic hydroxides;
- Compounds of normal acids with metallic peroxides;
- Compounds of peracids with metallic peroxides.

The elements of the fourth group of high atomic weight, and boron, yield peracids with hydrogen peroxide, and it is only elements of more non-metallic character—such as sulphur and carbon—which yield peracids by electrolysis.

It may be pointed out that in the peracids and their salts obtained by electrolysis the additional oxygen is directly attached to the nuclear negative atom or atoms, but that in salts of other peracids some at least of their special character is due to direct association of oxygen with the metal.

### SUB-GROUP VI A

#### *Chromium, Molybdenum, Tungsten, and Uranium*

As indicated in the introduction to Group VI, these elements, constituting a group of metals, do not display any close analogies with their congeners of sub-group B, except in the formation of the acidic trioxides  $\text{MO}_3$ .

In its chief basic oxide,  $\text{Cr}_2\text{O}_3$ , chromium is allied to aluminium and iron; thus, like aluminium hydroxide, chromic hydroxide,  $\text{Cr}(\text{OH})_3$ , is able to form salts with alkalis, the chromites, which are, however, considerably less stable than the aluminates, undergoing decomposition when their solutions are heated. Chromic sulphate, also, like the sulphates of aluminium and ferric iron, gives rise to alums.

These metals are not found native, but occur as oxides, such as  $\text{Cr}_2\text{O}_3$ , in chrome ironstone, and  $\text{U}_3\text{O}_8$ , pitchblende; as sulphides, such as  $\text{MoS}_2$ ; and as salts of the  $\text{H}_2\text{MO}_4$  acids, like  $\text{PbCrO}_4$ ,  $\text{PbMoO}_4$ , and  $\text{CaWO}_4$ .

They are prepared by the reduction of their oxides or chlorides by means of carbon, potassium cyanide, hydrogen, sodium, or aluminium;<sup>1</sup> and they are all metals of high melting-point and low atomic volume.

They combine directly on heating with oxygen, and with the halogens, forming with chlorine the volatile chlorides  $\text{CrCl}_3$ ,  $\text{MoCl}_5$ ,  $\text{WCl}_6$ ,  $\text{UCl}_4$ , of which  $\text{WCl}_6$  easily dissociates at

<sup>1</sup> The Goldschmidt process consists in firing a mixture of the oxide ( $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ , &c.) with aluminium powder by means of a suitable fuse. Owing to the great heat developed the process has been used in the welding of iron rails.



temperatures slightly above its boiling-point into  $\text{WCl}_5$  and chlorine.

### HALIDES

The halides are of numerous types, as will be seen from the table:—

	Fluorides	Chlorides	Bromides	Iodides
<b>Chromium.....</b>	$\text{CrF}_2, \text{CrF}_3$	$\text{CrCl}_2, \text{CrCl}_3$	$\text{CrBr}_2, \text{CrBr}_3$	$\text{CrI}_2, \text{CrI}_3$
<b>Molybdenum...</b>	$\text{MoF}_6$	$\left\{ \begin{array}{l} \text{MoCl}_2, \text{MoCl}_3 \\ \text{MoCl}_4, \text{MoCl}_5 \\ \text{MoCl}_4 (?) \end{array} \right\}$	$\left\{ \begin{array}{l} \text{MoBr}_2, \text{MoBr}_3 \\ \text{MoBr}_4 \end{array} \right\}$	$\left\{ \begin{array}{l} \text{MoI}_2, \text{MoI}_3 \\ \text{MoI}_4 \end{array} \right\}$
<b>Tungsten.....</b>	$\text{WF}_6$	$\left\{ \begin{array}{l} \text{WCl}_2, \text{WCl}_3 \\ \text{WCl}_4, \text{WCl}_5 \end{array} \right\}$	$\left\{ \begin{array}{l} \text{WBr}_2, \text{WBr}_3 \\ \text{WBr}_4 \end{array} \right\}$	$\left\{ \begin{array}{l} \text{WI}_2, \text{WI}_3 \\ \text{WI}_4 \end{array} \right\}$
<b>Uranium.....</b>	$\text{UF}_4$	$\left\{ \begin{array}{l} \text{UCl}_3, \text{UCl}_4 \\ \text{UCl}_5 \end{array} \right\}$	$\text{UBr}_4$	$\text{UI}_4$

A large number of oxyhalides are also known.

In addition to their formation by direct union, and by the solution of the metal or oxide in the halogen acid, many of the halides may be prepared by the action of a halogen on a heated mixture of oxide and carbon, as, for example:



The nature of these compounds is manifested:

- (i) By behaviour towards water,
- (ii) By volatility and solubility in non-hydroxylic solvents.

As an example the **chlorides of tungsten** may be considered.

The dichloride is a non-volatile, non-crystalline substance, which is slightly dissolved and easily decomposed by water, a higher oxide than corresponds to  $\text{WCl}_2$  separating, and hydrogen being evolved.

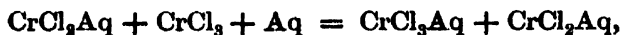
The tetrachloride is a grey crystalline powder which is non-volatile and infusible, but hygroscopic and partially decomposed by water.

The pentachloride crystallizes in black needles; it melts at  $248^\circ$  and boils at  $275.6^\circ$ . It is very hygroscopic, but largely decomposed by cold water. It is slightly soluble in carbon disulphide.

The hexachloride consists of dark-violet crystals which are

easily volatile, M.P.  $275^{\circ}$ , B.P.  $347^{\circ}$ . It is decomposed by boiling water, and is easily soluble in carbon disulphide.

None of these chlorides can be considered a well-defined salt, since even  $WCl_2$  manifests no characteristic saline properties towards water. The volatility and solubility in carbon disulphide of the higher chlorides, as well as the fact that they are decomposed by water into hydrochloric acid and an oxide, show them to be ill-defined chloranhydrides. The existence of numerous oxyhalides illustrates the same fact. The inertness of the lower halides of molybdenum and tungsten is remarkable, but the lower oxides show a similar inertness, being devoid of basic character, as will be seen later. That this inertness is not due only to lack of basigenic character in the metals is shown by the fact that chromous chloride is a true salt, soluble in water and crystallising with water of crystallisation, while chromic chloride is inert when prepared in the anhydrous condition by heating a mixture of chromic oxide and carbon in a current of chlorine. The presence, however, of a trace of chromous (cuprous or stannous) chloride effects solution, thus:—



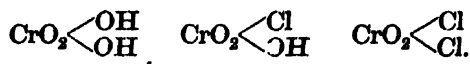
the  $CrCl_2.Aq$  being oxidized by the solid  $CrCl_3$  to  $CrCl_3.Aq$ , the reduced chloride thus passing into solution as  $CrCl_2.Aq$ .  $CrCl_3$  may be obtained from this solution in a soluble crystalline form as  $CrCl_3 \cdot 6H_2O$ .

In this form chromic chloride is analogous to ferric chloride, and may therefore be considered as the chloride of a weak base. Chromic chloride further resembles aluminium and ferric chlorides by forming double salts with alkali chlorides, such as  $CrCl_3 \cdot 2KCl \cdot 2H_2O$ .

Chromium forms no higher chlorides, so does not furnish a chloranhydride of an orthoacid. Like sulphur it forms an oxychloride, the chloride of a meta-acid, chromyl chloride,  $CrO_2Cl_2$ . This compound, prepared by heating together potassium dichromate, sodium chloride, and sulphuric acid, is a dark-red liquid, boiling at  $116^{\circ}$ , and is analogous to sulphuryl chloride,  $SO_2Cl_2$ . It forms chromic and hydrochloric acids

with water; but salts of the intermediate chlorochromic acid, analogous to chlorosulphonic acid, are known, and are formed when concentrated hydrochloric acid acts on a dichromate.

Chromic acid, chlorochromic acid, and chromyl chloride are thus related to one another:—



It is instructive to observe that while chromyl fluoride,  $\text{CrO}_2\text{F}_2$ , is known, the bromide and iodide do not exist.

The oxyhalides of the same type formed by the other metals of the group do not so readily undergo resolution by water;  $\text{UO}_2\text{Cl}_2$ , for instance, is quite stable, and may be regarded as a uranyl salt. The solubility of this latter compound in alcohol and ether, however, and its power of combination with alkali chlorides and the hydrochlorides of organic bases, reveal acidic character.

#### OXIDES

The oxides of Group VIA metals are numerous, like the halides. The principal ones are classified in the subjoined table:

Chromium...	$\text{CrO}$	$\text{Cr}_2\text{O}_3$	$\text{CrO}_3$	$\text{CrO}_4(+3\text{NH}_3)$
Molybdenum	$\text{MoO}(\text{hydrated})$	$\text{Mo}_2\text{O}_3$	$\text{MoO}_2$	$\text{MoO}_3$
Tungsten.....	—	—	$\text{WO}_2$	$\text{WO}_3$
Uranium.....	—	—	$\text{UO}_2$	$\text{UO}_3$

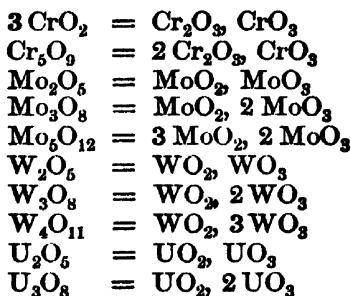
Of oxides of the type  $\text{MO}$ , examples are known in the case of chromium and molybdenum only.  $\text{Cr}(\text{OH})_2$  is a true base, dissolving in acids to form the chromous salts; hydrated  $\text{MoO}$  possesses feebly basic properties. Of the sesquioxides,  $\text{M}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$  is a basic oxide possessing feebly acidic properties,  $\text{Mo}_2\text{O}_3$  shows no acidic properties, and its basic functions are ill defined since it is insoluble in acids, and even the hydroxide dissolves with difficulty.

Of the dioxides,  $\text{MoO}_2$  forms very unstable salts; the hydroxide  $\text{Mo}(\text{OH})_4$  dissolves slowly in water, forming an acid solution.  $\text{WO}_2$  is slightly soluble in concentrated hydrochloric and sulphuric acids, forming purple solutions which possibly contain tungstous salts. As was pointed out when dealing with the chlorides, molybdenum and tungsten oxides show a

remarkable inability to form salts with acids.  $\text{UO}_2$ , uranous oxide, corresponds with uranous salts of the type  $\text{UX}_4$ . The oxides  $\text{MO}_3$  are all acidic; but  $\text{UO}_3$  is sufficiently basic to form the uranyl salts  $\text{UO}_2\text{X}_2$ .

$\text{CrO}_4$  and  $\text{UO}_4$  are peroxides resulting from the action of hydrogen peroxide on chromates and uranates. (See Appendix to Group VI B.)

In addition to the above oxides a number of complex oxides exist, which, in the case of chromium, are compounds of  $\text{Cr}_2\text{O}_3$  and  $\text{CrO}_3$ , and, in the case of the other metals, of  $\text{MO}_2$  and  $\text{MO}_3$ . The following are the more important of these complex oxides:—



#### COMPOUNDS CORRESPONDING TO THE VARIOUS OXIDES

**Chromous salts**, corresponding to the oxide  $\text{CrO}$ , are prepared by the reduction of acidified solutions of chromic salts or chromates in absence of air. They are white when anhydrous and blue when hydrated. They oxidize with the greatest ease, forming, when solid, basic chromic salts. A blue solution containing a chromous salt on exposure to air rapidly turns green, by formation of chromic salt. The acetate is the most stable salt; the sulphate,  $\text{CrSO}_4 \cdot 7\text{H}_2\text{O}$ , is isomorphous with ferrous sulphate, and forms the double salt  $\text{CrSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ .

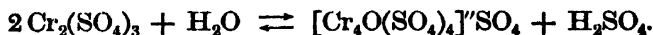
The oxide  $\text{MoO}$  gives rise to no salts.

The **chromic salts**, corresponding with the oxide  $\text{Cr}_2\text{O}_3$  and the hydroxide  $\text{Cr}(\text{OH})_3$ , are usually prepared from chromates by reduction:



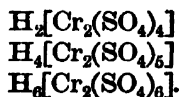
Thus from potassium dichromate and sulphuric acid, on reduction by alcohol or sulphurous acid, or by nascent hydrogen, as in the bichromate cell, the alum  $K_2SO_4$ ,  $Cr_2(SO_4)_3$ ,  $24 H_2O$ , is formed.

Crystals of **chromic alum**, as well as of **chromic sulphate**,  $Cr_2(SO_4)_3$ ,  $18 H_2O$ , are violet. Cold solutions of these salts are violet, but when heated they turn green. After cooling and prolonged standing the violet colour returns. Only one-third of the sulphate present in the green solution can be precipitated by barium chloride, the remaining two-thirds being present in a complex basic ion. The following equation represents the change:—



The complex green substance is known as **sulphochromyl sulphate**.

Chromic sulphate or alum may, however, undergo a different change. When its crystals are heated to  $90^\circ$  they lose some water and turn green. The product is soluble in water, producing a green solution which gives no precipitate with barium chloride. The substance thus obtained from chromic alum is isomeric therewith, and consists of **potassium chromisulphate**,  $K_2[Cr_2(SO_4)_4]$  (*cf.* potassium chromite,  $K_2Cr_2O_4$ ). The following solid **chromisulphuric acids** may be obtained as the result of warming chromic sulphate with sulphuric acid:—



The last, which may be considered as orthochromisulphuric acid, is analogous to orthosulphuric acid. The fact that chromium, in a state of oxidation corresponding to  $Cr_2O_3$ , may form part of either a basic or an acidic complex is well illustrated by the above compounds. It has already been noticed that the oxide  $Cr_2O_3$  partakes of this same intermediate character.

**Chromic chloride**,  $CrCl_3$ , when prepared in the dry way, consists of pink scales which are insoluble in water and chemically inert. In the solid hydrated condition, as  $CrCl_3 \cdot 6H_2O$ ,

as well as in solution, it exists both in violet and green forms. The amount of chlorine in the green solution which can be precipitated by silver is variable, some of it having entered the basic ion forming  $[\text{CrCl}]'\text{Cl}_2$  or  $[\text{CrCl}_2]'\text{Cl}$ . The green solution turns violet on long standing, and at the same time almost all the chlorine becomes ionic.

**Chromic sulphide**, like aluminium sulphide, can only be formed in the dry way, and is hydrolysed by water.

Of salts corresponding to the **oxides**  $\text{MO}_2$ , those of uranium, the **uranous salts**, are the only ones to be considered. These salts, which are obtained in solution by the reduction of an acidified uranyl solution with zinc, are green, and yield green crystals; *e.g.*  $\text{UCl}_4$  and  $\text{U}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$ . The sulphate also results, together with uranyl sulphate, when pitchblende,  $\text{U}_3\text{O}_8$ , is acted on by sulphuric acid,



Like the chromous salts, the uranous salts are powerful reducing agents. Thus the chloride, formed when chlorine acts on uranium, reduces ferric to ferrous salts, and precipitates gold and silver.

As previously mentioned, the **oxides**  $\text{RO}_3$  are chiefly acidic;  $\text{MoO}_3$  exhibits feebly, and  $\text{UO}_3$  more powerfully basic properties. The acids cannot be obtained in a pure state by combination of the oxides with water.  $\text{CrO}_3$  is a red crystalline substance easily soluble in water; this solution contains dichromic acid,  $\text{H}_2\text{Cr}_2\text{O}_7$ , but on evaporation crystals of the anhydride, and not the acid, separate.  $\text{MoO}_3$  is very slightly soluble in water, yielding a solution which reacts acid;  $\text{WO}_3$  and  $\text{UO}_3$  are insoluble in water, but  $\text{WO}_3$  is soluble in boiling aqueous alkalis.

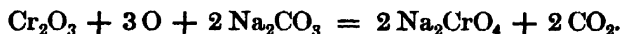
#### ACIDS DERIVED FROM $\text{MO}_3$ , AND THEIR SALTS

**Acids** of the type  $\text{H}_2\text{MO}_4$  are known in the case of molybdenum, tungsten, and uranium.

**Molybdic acid**,  $\text{H}_2\text{MoO}_4$ , is a white, crystalline powder obtained when a nitric-acid solution of  $\text{MoO}_3$  evaporates

spontaneously. The hydrate,  $\text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ , crystallizes in yellow crusts from a nitric-acid solution of ammonium molybdate. **Tungstic acid**,  $\text{H}_2\text{WO}_4$ , is a yellow powder insoluble in water and most acids.  $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ , soluble in water, is obtained by precipitating a tungstate by acid in the cold. Hydrated **uranic acid**,  $\text{H}_2\text{UO}_4 \cdot \text{H}_2\text{O}$ , is obtained as a yellow mass by evaporating a solution of uranyl nitrate,  $\text{UO}_2(\text{NO}_3)_2$ , in alcohol.

**Salts** of the type  $\text{R}_2\text{MO}_4$  are known for all four elements; only the **chromates** are important. The alkali chromates are lemon yellow, and are obtained by the action of alkalis and oxidizing agents on chromic oxide; thus:—



When a chromate is prepared by fusion, the oxygen may be supplied either from potassium chlorate or nitrate, or from the atmosphere. In the wet way precipitated chromic hydroxide may be oxidized by alkaline hydrogen peroxide, produced from sodium peroxide, by hypochlorites, or by lead peroxide.

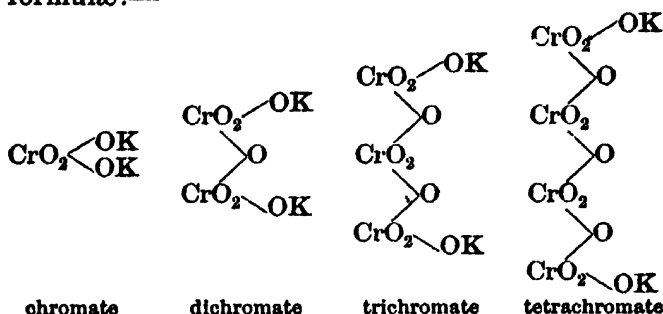
**Condensed acids and their salts.**—It was observed in the case of sulphuric acid and its salts that condensation of two molecules may take place under certain conditions to form disulphates. A similar phenomenon is noticed with other oxyacids, such as phosphoric, iodic, and boric, but is unknown with nitric acid. It is specially characteristic of the weak oxyacids of Group VIA, so that indeed the more complex acids and their salts are for the most part obtained more readily than the simple ones.

When normal chromates are treated with acids, **dichromates** are formed, thus:—



Potassium dichromate, in turn, yields, with chromic anhydride, or on boiling with moderately concentrated nitric acid, the **trichromate**  $\text{K}_2\text{Cr}_3\text{O}_{10}$ ; and this, again, with concentrated nitric acid, gives the **tetrachromate**  $\text{K}_2\text{Cr}_4\text{O}_{13}$ .

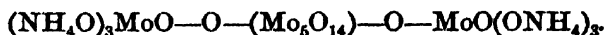
These salts may be represented by the following constitutional formulæ:—



Water hydrolyses tri- and tetrachromates to dichromates and chromic acid, and excess of alkali reconverts all the condensed chromates to the normal salts.

Molybdic and tungstic acids are more, and uranic acid less, prone to condensation than chromic acid.

The general formula for **complex molybdates** may be written  $\text{R}'_2\text{O}, x\text{MoO}_3$ , where  $x = 1, 2, 3, 4, 7, 8$ , or  $10$ . Trimolybdates are common. There are also salts derived from condensation of the next hydrated acid,  $\text{H}_4\text{MoO}_5$ ; ordinary ammonium molybdate, for instance, is  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ; its constitution probably being

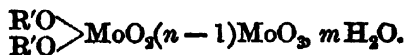


The **polytungstates** are even more complex than the polymolybdates. Tetratungstic acid,  $\text{H}_2\text{W}_4\text{O}_{18} \cdot 7\text{H}_2\text{O}$ , is a crystalline body which is soluble in water. Commercial sodium tungstate possesses the composition  $\text{Na}_{10}\text{W}_{12}\text{O}_{41} \cdot 28\text{H}_2\text{O}$  ( $\text{Na}_{10}\text{W}_{12}\text{O}_{41} = 5\text{Na}_2\text{O}, 12\text{WO}_3$ ).

In addition to the above method of condensation, molybdic and tungstic acids likewise possess the power of combining with phosphoric and other acids of a similar type to form complex acids. Consider the molybdate

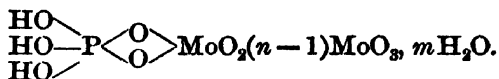


which may be written





The acid corresponding to this salt, on condensation with phosphoric acid, will produce

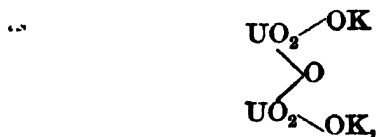


Ammonium phosphomolybdate, in which  $n = 12$  and  $m = 0$ , is  $(\text{NH}_4)_3\text{MoPO}_7, 11\text{MoO}_3$ . It is the yellow precipitate produced in the well-known molybdate test for phosphoric acid. The corresponding compound with arsenic acid is formed at a higher temperature, probably on account of the feebler acidic character of arsenic acid. The following is a list of the chief complex acids of molybdenum and tungsten. In most cases combinations in various proportions are known:—

Phosphomolybdic <sup>1</sup> acids			Phosphotungstic <sup>1</sup> acids		
Arseno-	"	"	Arseno-	"	"
Arseni-	"	"	Arseni-	"	"
Iodi-	"	"	Vanadi-	"	"
Periodi-	"	"	Silici-	"	"
Vanadi-	"	"			
Silici-	"	"			

Chromium forms few of such compounds, and uranium none.

The chief **uranates** are derived from the acid  $\text{H}_2\text{U}_2\text{O}_7$ . When potassium hydroxide is added to uranyl nitrate solution,  $\text{UO}_2(\text{NO}_3)_2$ , the yellow precipitate obtained consists of uranyl hydroxide together with some potassium diuranate,



which is thus insoluble in water. The sodium salt,  $\text{Na}_2\text{U}_2\text{O}_7, 6\text{H}_2\text{O}$ , is uranium yellow; glass coloured with this substance is bright yellow, and shows a green fluorescence. Tri- and tetra- as well as monouranates are known.

Reference has previously been made to **uranyl salts**. The existence of these salts is due to the fact that uranium tri-

<sup>1</sup> These would be better described as phosphori-molybdic and -tungstic acids respectively.

oxide, alone among trioxides, possesses distinctly basic properties. This is due to the superior metallic character of uranium, a fact indicated by its high atomic weight and position as the last member of Group VIA of the periodic table. One only of the three oxygen atoms can, however, be replaced by acid radicles; and thus basic salts, known as the uranyl salts, result.

The nitrate,  $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ , is the best-known salt. It is yellow and possesses a green fluorescence. Certain organic salts, such as the oxalate, are sensitive to light, being thus reducible to uranous compounds. Uranyl ammonium phosphate,  $\text{UO}_2\text{NH}_4\text{PO}_4$ , is a greenish-yellow precipitate, insoluble in acetic acid; it is obtained in a process for the volumetric estimation of phosphates. The ferrocyanide is a brown precipitate.

Chromium forms series of complex cyanides and ammines, which will be dealt with under Group VIII.

## CHAPTER XI

### GROUP VII

#### SUB-GROUP A

(Mn) (54.93)

—  
—  
•  
—

#### SUB-GROUP B

F (19.0)  
Cl (35.46)

Br (79.92)  
I (126.92)

—  
—  
—

### THE HALOGEN ELEMENTS

*Fluorine, Chlorine, Bromine, and Iodine.*

Of the five known members of the seventh group, the four halogen elements, fluorine, chlorine, bromine, and iodine, form a family of closely allied elements; whilst manganese, the sole representative of the even series in the periodic table, is in most respects quite dissimilar from them.

Fluorine is the most electro-negative of all the elements, and the characteristics of the halogens as a class are almost entirely electro-negative and oxygenic. This is in accordance with the positions which they occupy as terminal members of the various periods.

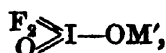
There is an increase of electro-positiveness from fluorine through chlorine and bromine to iodine, and a corresponding decrease in chemical activity towards hydrogen and all elements which manifest any electro-positive properties.

The extraordinary affinity of fluorine for hydrogen, which is manifested by its power of combining with this element in the dark, and displacing chlorine from hydrogen chloride, is accompanied by complete inability to combine with oxygen under any circumstances. Thus it would appear that the atoms of this extremely electro-negative element, although combining with one another in pairs to form molecules, lack ability to combine with the atoms of those elements which approach nearest to it in electro-negative properties, and are therefore its neighbours in the periodic system.

An enquiry into the power of fluorine to combine with electro-negative elements yields the following results.

Though yielding no compound with oxygen, fluorine forms hexafluorides with sulphur, selenium, and tellurium; the fluorides of sulphurous and sulphuric acids,  $\text{SOF}_2$  and  $\text{SO}_2\text{F}_2$ , are likewise known, as well as fluorsulphonic acid,  $\text{SO}_2 \cdot \text{F} \cdot \text{OH}$ .

Nitrogen probably forms an unstable fluoride,  $\text{NF}_3$ , whilst fluorides of the other elements of the fifth group are well known. Fluorine does not form any compound with chlorine, though  $\text{BrF}_3$  and  $\text{IF}_5$  are known; and also salts of the alkali metals of the type



the difluoriodates, have been prepared, in which fluorine is joined directly to iodine. Analogous derivatives of chloric and bromic acids do not exist. Fluorine does not unite directly with gold or platinum, although these metals are attacked by chlorine.

Thus, by inspection of the periodic table, a certain restricted area around fluorine is discovered which contains those elements with which fluorine forms no compounds.

The stability of the compounds which the halogens form with oxygen increases from chlorine to iodine, though in some at least of its reactions bromine shows less affinity for oxygen than chlorine. Thus the superior affinity of iodine for oxygen is shown by the fact that it displaces chlorine from potassium chlorate according to the reaction



and also by the direct oxidation of iodine to iodic acid by means of nitric acid. This increase in stability of oxygen compounds, with rising atomic weight, is the opposite of what obtains in Group VI B.

With reference to the compounds of the halogens with each other it may be remarked that, whilst bromine is not known to form a compound with chlorine, iodine forms the compounds  $\text{ICl}$  and  $\text{ICl}_3$ , though with bromine only the monobromide  $\text{IBr}$  is known. It will be observed that the power possessed by the halogens of forming compounds with one another depends upon the electro-chemical difference between the atoms forming the compounds.

#### PREPARATION OF THE HALOGENS

The following methods are available:—

- (i) Oxidation of the hydracid in aqueous solution.
- (ii) Electrolysis of halides under conditions favourable to the isolation of the element, secondary reactions being guarded against.
- (iii) The decomposition of a perhalide by heat, just as oxygen is obtained by the decomposition of manganese or lead peroxide.

(i) The oxidation of a hydracid according to the reaction



depends upon the degree of affinity of the halogen element for hydrogen. Now, since fluorine combines with hydrogen in

the dark, and decomposes water instantly, it is not to be expected that this element will be obtained by the above reaction. The other halogens, however, in accordance with their decrease in electro-negativeness from chlorine to iodine, may be prepared by the use of oxidizing agents with increasing ease. If a mixture of air or oxygen with the moist hydracid is passed through a heated tube, no change takes place in the case of hydrofluoric acid, partial oxidation with hydrochloric acid, and more rapid and complete action with hydrobromic and hydriodic acids. When the moist hydracids are mixed with oxygen and exposed to sunlight the reaction extends from zero with hydrofluoric to a maximum with hydriodic acid, the same being true of solutions of the acids in water. This gradation of oxidizability is further illustrated by the fact that sulphuric acid, which does not oxidize hydrogen chloride, liberates bromine and iodine from their hydracids when the latter are prepared by warming this acid with bromides and iodides respectively. The possibility of the reverse action, in which the free element decomposes water, diminishes rapidly on passing from fluorine to the other halogens. Upon this diminution depends the loss of bleaching power on passing from chlorine to bromine and iodine.

(ii) Whilst chlorine, as well as bromine and iodine, can be obtained by the electrolysis of aqueous solutions of the corresponding alkali halides, it is obvious that fluorine cannot be obtained by this method in the presence of water. The means by which Moissan, in 1886, obtained fluorine consisted in the application of this powerful method of decomposition to a solution of potassium fluoride in anhydrous hydrofluoric acid, such a solution being an anhydrous electrolyte.

(iii) The applicability of the third method depends upon the existence of polyhalides of certain elements which are more stable at low than at high temperatures. Considering fluorine, for instance, and the compounds it forms with elements from the first group onwards; whilst the mono-, di-, and trifluorides of the first three groups respectively will not undergo such decomposition, in the fourth group a condition

is reached in which the atoms of certain elements, whilst forming tetrafluorides, do not manifest sufficient affinity for fluorine to retain four atoms in combination at high temperatures. Thus cerium tetrafluoride was found by Brauner, in 1882, to break up, when heated, into fluorine and a lower fluoride. Fluorine was also obtained later by the same chemist by the action of heat on potassium hydrogen fluorplumbate,



In the same way  $\text{PbCl}_4$  easily breaks up into  $\text{PbCl}_2$  and  $\text{Cl}_2$ , and in the familiar process for the preparation of chlorine from manganese dioxide and hydrochloric acid, manganic chloride,  $\text{MnCl}_3$ , is formed as an intermediate product which breaks up into manganous chloride and chlorine when heated.

An examination of the physical properties of the halogen elements, as given in the table on the following page, shows a regular gradation from fluorine to iodine. This is manifested in the rise of melting and boiling points, and in deepening colour; the densities of the liquid elements likewise increase in the same order. Solubility in water, however, diminishes from chlorine to iodine. Power of dissociation of the diatomic molecules into atoms by heat, increases from fluorine to iodine. No dissociation has been observed in the case of fluorine gas; chlorine manifests a sensible diminution in density at  $1400^\circ$ ; the density of bromine vapour becomes two-thirds of its normal value at  $1570^\circ$ ; whilst in the case of iodine the density of the vapour begins to diminish at  $700^\circ$  and becomes half its normal value at  $1700^\circ$ , above which temperature the element exists in the atomic state.

This increase in readiness to dissociate with rise of atomic weight and increase in electro-positiveness, is consistent with an approximation to the character of metallic vapours, which, as far as observation goes, appear to exist in a monatomic state.

Relationships between the chemical characters of these elements appear in the study of their compounds. More chemical differences will be observed between fluorine and chlorine

## SUMMARY OF GROUP VII

Properties of Element.	F	Cl	Br	I	Mn
Atomic weight.....	19.0	35.46	79.92	126.92	54.93
Appearance.....	{ pale greenish-yellow gas - 223°	greenish-yellow gas - 102°	deep reddish-brown liquid - 7.3°	violet-black solid with metallic lustre }	lustrous metal
Melting-point.....	- 223°	- 102°	- 7.3°	114°	1245°
Boiling-point at atm. pressure.....	- 187°	- 33.6°	58-59°	184°	—
Density of liquid.....	1.14 (at B.P.)	1.507 (at B.P.)	2.982 (at B.P.)	4.95	—
Density of solid.....	—	> 1.66 (at M.P.)	—	—	8.0
<i>Types of compounds.</i>					
Hydrides HX.....	HF(H <sub>2</sub> F <sub>2</sub> )	HCl	HBr	HI	—
Oxides and hydroxides—	—	Cl <sub>2</sub> O	—	—	—
X <sub>2</sub> O.....	—	*ClOH	*BrOH	*IOH	MnO (basic)
XO.....	—	—	—	—	Mn <sub>2</sub> O <sub>3</sub> (neutral)
X <sub>2</sub> O <sub>3</sub> .....	—	—	—	—	Mn <sub>2</sub> O <sub>3</sub> (basic)
XO <sub>2</sub> .....	—	*ClOOH	—	—	MnOOH (basic)
XOOH.....	—	{ ClO <sub>2</sub> (mixed) { anhydride }	—	IOCl <sub>2</sub> H <sub>2</sub> (basic oxide)	{ MnO <sub>2</sub> (functions various)
XO <sub>2</sub> .....	—	*ClO <sub>2</sub> OH	—	(I <sub>2</sub> O <sub>4</sub> )	—
X <sub>2</sub> O <sub>4</sub> .....	—	—	*BrO <sub>2</sub> OH	I <sub>2</sub> O <sub>3</sub>	—
XO <sub>2</sub> OH.....	—	—	—	{ IO <sub>2</sub> C <sub>2</sub> H <sub>2</sub> (basic peroxide) }	—
XO <sub>3</sub> .....	—	—	—	—	—
XO.....	—	—	—	—	MnO <sub>2</sub> (acidic)
X <sub>2</sub> O(OH) <sub>2</sub> .....	—	—	—	—	Mn <sub>2</sub> O <sub>4</sub> (OH) <sub>2</sub>
X <sub>2</sub> O.....	—	Cl <sub>2</sub> O <sub>7</sub>	—	I <sub>2</sub> O <sub>7</sub>	Mn <sub>2</sub> O <sub>7</sub> (OK) <sub>2</sub>
XO <sub>2</sub> OH.....	—	ClO <sub>3</sub> OH	—	{ IO <sub>2</sub> OH (and other forms) }	Mn <sub>2</sub> O <sub>7</sub> (acidic)
B <sub>2</sub> XOH.....	—	—	—	B <sub>2</sub> IOH (iodonium)	Mn <sub>2</sub> O <sub>3</sub> OH

\*Known only in solution.

than between the other successive members of the group; it has previously been seen that the properties of the first member of a group are somewhat exceptional. Chlorine, bromine, and iodine, indeed, form a triad of elements, the atomic weight of bromine standing midway between those of chlorine and iodine. Fluorine stands outside this triad by reason of many of its properties. This is illustrated in the following table of atomic weights and differences:—

		Difference.
F.....	19.0	16.46
Cl.....	35.46	44.46
Br.....	79.92	47.00
I.....	126.92	

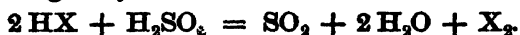
#### HALOGEN HYDRACIDS AND THEIR SALTS

Of the hydracids of the four halogen elements hydrofluoric acid is the most and hydriodic acid the least stable. The heats of formation of these four compounds from their elements are:—

HF.....	389 K
HCl.....	220 K
HBr.....	84 K
HI.....	—60 K

These figures represent the relative stabilities of the four acids. Fluorine will therefore displace chlorine, bromine, and iodine from their compounds with hydrogen or metals, chlorine will displace bromine and iodine, and bromine will displace iodine only.

Reference has already been made to the fact that hydrobromic and hydriodic acids cannot be obtained pure by the action of concentrated sulphuric acid upon the corresponding alkali salts. Bromine and iodine respectively are liberated owing to the oxidation of the hydracids by sulphuric acid in the following way:—

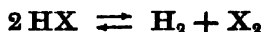


This is quite in accord with what has just been learned regarding the instability of these acids.

These reactions are reversible, however, hydrobromic and hydriodic acids being produced by interaction of halogen and sulphurous acid.

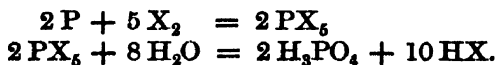


Hydrogen bromide, and more especially hydrogen iodide, are therefore reducing agents, because of the ease with which they separate into their elements at moderate temperatures. A consideration of the reversible reaction



shows that the reaction from left to right, which is almost if not quite non-existent in the case of fluorine, increases in ease regularly through chlorine and bromine to iodine. Such dissociation, which constitutes an ordinary reversible reaction in the absence of an oxidizing agent, is however promoted by sulphuric acid and other substances which have the power of removing hydrogen from the hydracid, thereby becoming reduced.

This decomposition of hydrobromic and hydriodic acids is avoided by substituting phosphoric for sulphuric acid in their preparation, or by the method in which the element is made to react with red phosphorus and water:



Whilst hydrogen fluoride resembles hydrogen chloride in its manner of preparation and some of its properties, it differs from the latter, and from the other halogen acids, both in its physical properties and in the nature of the salts which it forms. Hydrogen fluoride boils at  $19.4^\circ$  under atmospheric pressure, whilst the boiling-points of hydrogen chloride, bromide, and iodide are respectively  $-83.7^\circ$ ,  $-64.9^\circ$ , and  $-34.1^\circ$ .

This difference is to be explained by the fact that the molecules of hydrogen fluoride exhibit a tendency towards polymerisation, so that the molecular weight of this compound is found to be even greater than that of hydrogen chloride under similar circumstances. It has been concluded, moreover, from vapour-density determinations of hydrogen fluoride gas taken at about  $30^\circ$ , that the molecular formula should be  $\text{H}_2\text{F}_2$ ; and it is probably greater than this at lower temperatures. It is not surprising, therefore, that acid salts such

as  $\text{KHF}_2$  exist, and that they are broken up by heat. Probably fluorine is at least trivalent in such compounds; and it is remarkable that whilst the other halogens exhibit polyvalency in their oxygen compounds, fluorine, which forms no compounds with oxygen, yet becomes polyvalent in its compound with hydrogen. A difference between hydrofluoric and the other hydracids is also illustrated by the existence of such stable compounds as  $\text{H}_2\text{SiF}_6$ ,  $\text{HBF}_4$ .

It must further be observed that the fluorides of certain metals differ from the corresponding chlorides, bromides, and iodides. Calcium fluoride, for instance, is insoluble in water, whilst the chloride, bromide, and iodide of this metal are soluble; and, on the other hand, silver fluoride is a soluble, deliquescent salt in contradistinction to the other halides of silver, which are insoluble in water. Mercuric fluoride, too, differs from the chloride, bromide, and iodide in being completely hydrolysed by water, thus resembling the oxy salts of this metal.

The solubilities of the hydracids in water are as follows, the figures representing the weight of acid which dissolves in 1 gram of water at  $10^\circ \text{C}$ .:—

HF.....	very soluble
HCl.....	0.77
HBr.....	2.10
HI.....	2.48

Again it is seen that hydrofluoric acid is exceptional, its greater solubility being probably connected with its greater condensibility.

Lastly, the relative strengths of the halogen hydracids must be considered.

The following table gives the heats of neutralisation and the avidities as determined by Thomsen:—

	Heat of Neutralisation		"Avidity"
HF.....	163 K	.....	0.05
HCl.....	137 K	.....	1.00
HBr.....	138 K	.....	0.89
HI.....	137 K	.....	0.70

The degree of electrolytic dissociation of these acids at different states of dilution is given by the following table (Ostwald):—

Dilution	HF	HCl	HBr	HI
10 litres.....	0.10	0.95	0.95	0.95
100 litres.....	0.26	0.98	0.98	0.98
1000 litres.....	0.59	0.99	0.99	0.99

Since the strength of an acid is indicated by the degree of its electrolytic dissociation at a given dilution, it is manifest that whilst HCl, HBr, and HI are strong acids of about equal strength, HF is a much weaker acid. The values for avidity obtained by Thomsen indicate the same fact. Thus hydrofluoric acid is largely displaced from sodium fluoride by the stronger hydrochloric acid. It is important, therefore, to recognize that the relative strengths of these acids are not in the order of the electro-negativeness of the halogen elements which they contain, or of their relative stability. The weakness of hydrofluoric acid is at first sight surprising, since it would be thought that such an extremely active and electro-negative element as fluorine must needs produce a powerful acid. Now if an atom of fluorine were a constituent of the molecule of an oxyacid, it would no doubt by its presence promote the separation of hydrogen ions just as chlorine does in the chloracetic acids, the strength of the acid thus being ~~increased~~ by substitution. In the case of hydrofluoric acid, however, the fluorine atom is united directly to the hydrogen atom of the acid; and it may be on account of the extraordinary affinity of fluorine for hydrogen that this acid is imperfectly ionised in solution.

The excess of heat of neutralisation of hydrofluoric acid over 137 K (viz. 26 K) is the heat evolved by the acid in reaching a state of complete ionisation in solution during the process of neutralisation.

## OXIDES AND OXYACIDS OF CHLORINE, BROMINE, AND IODINE

The following are the types of oxyacids formed by these elements:—

HOX, *e.g.* hypochlorous acid HOCl

HOXO, *e.g.* chlorous acid HOClO or HClO<sub>2</sub>

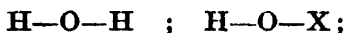
HOXO<sub>2</sub>, *e.g.* chloric acid HOClO<sub>2</sub> or HClO<sub>3</sub>

HOXO<sub>3</sub>, *e.g.* perchloric acid HOClO<sub>3</sub> or HOCIO<sub>4</sub>.

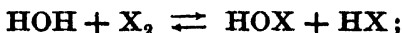
Only in the case of chlorine is the series complete; bromous acid probably exists, but not perbromic acid, HBrO<sub>4</sub>; iodosous acid, HIO<sub>2</sub>, is unknown.

Of the anhydrides corresponding to these acids, namely X<sub>2</sub>O, X<sub>2</sub>O<sub>3</sub>, X<sub>2</sub>O<sub>5</sub>, and X<sub>2</sub>O<sub>7</sub> respectively, chlorine forms Cl<sub>2</sub>O and Cl<sub>2</sub>O<sub>7</sub>, iodine I<sub>2</sub>O<sub>5</sub> and possibly I<sub>2</sub>O<sub>7</sub>, whilst bromine forms no oxide. In addition, chlorine forms the mixed anhydride ClO<sub>2</sub>.

Acids of the type HOX are weak and unstable. On account of their feebly acidic character they may be represented as derivatives of water,<sup>1</sup> in which one hydrogen atom is replaced by halogen thus:—



and indeed halogen can displace hydrogen from water itself to some extent according to the reaction



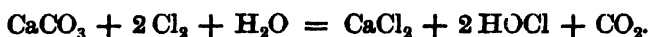
and if cold dilute alkali is employed, so that the acids produced are neutralised, the change is completed according to the equation



The weakness of these acids is further shown by the fact that

<sup>1</sup> To the view that the weakness of, *e.g.* HOCl may be attributed to the fact of its being a derivative of water it might be objected that potash and soda, being likewise derivatives of water, are strong bases. The cases, however, are not parallel, since the halogen has to cause the separation of H ions and the alkali metal of OH ions. No single element, indeed, in combination with hydroxyl alone is known to form a powerful oxyacid. The presence of adjacent negative atoms or groups combined with an element is necessary before any considerable separation of hydrogen ions occurs.

they are completely displaced from combination by such weak acids as carbonic and acetic acids. If, accordingly, chlorine gas is passed through water containing finely-divided chalk in suspension, whilst the hydrochloric acid formed by the action of the chlorine upon the water is neutralised by the chalk, the **hypochlorous acid** produced at the same time remains uncombined:

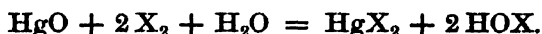


If sodium sulphate is substituted for calcium carbonate the reaction may be represented as follows:—

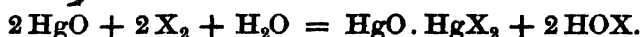


the fixation of the hydrochloric acid by reaction with  $\text{Na}_2\text{SO}_4$  allowing of the formation of HOCl in quantity. Hypochlorous acid may be conveniently prepared in solution by distilling a hypochlorite with dilute nitric acid.

A general method for the preparation of acids of the type HOX consists in digesting the halogen and water with powdered mercuric oxide, the following reaction taking place:—



If excess of mercuric oxide is employed, an insoluble basic halide is formed, and a pure solution of the acid obtained by filtration, thus:—

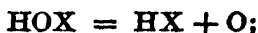


The oxide of mercury serves the purpose of removing the HX acid from the system, the HOX acids not being sufficiently strong to form salts with this oxide.

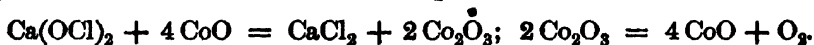
Owing to their instability none of these acids has been obtained pure; but solid **calcium hypochlorite** results when chlorine is passed into milk of lime, and the resulting solution is evaporated under reduced pressure. The dried salt is more efficient than bleaching-powder.

The stability of acids of the type HOX diminishes from chlorine to iodine, just as the stability of the hydracids themselves diminishes. Hypoiodous acid is, however, much less

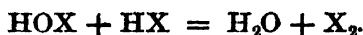
stable than the other two, and cannot be distilled. The instability of these acids depends first of all upon a tendency to split off oxygen thus:—



the preparation of this gas from bleaching-powder by the catalytic action of cobaltous oxide depends on this reaction:—



Hydracid also separates halogen in the following way:—



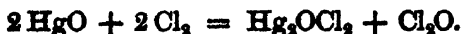
The acids themselves, therefore, may yield halogen as well as oxygen by spontaneous decomposition, but when liberated from their salts by excess of halogen acid, halogen only will be evolved. Instead, however, of being evolved in the gaseous state, the oxygen liberated in the decomposition of HOX acid may oxidize the acid itself, producing a higher oxyacid of the type  $\text{HOXO}_2$ . Salts of these acids especially are produced when alkali hypochlorites are decomposed by heat, there being no free hydracid to cause evolution of halogen; thus:—



This tendency towards the formation of salts of the type  $\text{MOXO}_2$  is increased by excess of halogen, and diminished by excess of alkali. The formation of chlorate by the action of excess of chlorine accounts for the occasional spoiling of bleaching-powder in the process of manufacture.

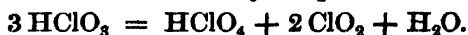
The tendency of hypoiodite to pass into iodide and iodate is much greater than in the case of the corresponding chlorine and bromine compounds, as will be seen later.

**Anhydride of the type  $\text{X}_2\text{O}$ .**—Chlorine monoxide,  $\text{Cl}_2\text{O}$ , is the only compound of this type which exists; and just as hypochlorous acid is prepared by the action of chlorine on mercuric oxide and water, so its anhydride is formed when chlorine reacts with dry mercuric oxide, thus:—

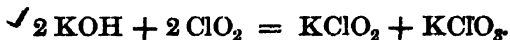


Chlorine monoxide is an unstable gas which yields hypochlorous acid with water. The non-formation of bromine and iodine monoxides may be connected with the less stability of hypobromous and hypoiodous acids, as compared with hypochlorous acid; in this case the anhydrides are less stable than the corresponding acids, though this is by no means generally the case. Sulphur dioxide, for instance, is more stable than sulphur trioxide, though 'sulphuric is much more stable than sulphurous acid. Carbonic and chromic anhydrides are likewise much more stable than the corresponding acids. There appears, therefore, to be no simple connection between the stabilities of an acid and of its anhydride.

**Dioxides  $\text{XO}_2$ .**—Chlorine and iodine form dioxides. **Chlorine dioxide** or **peroxide** is a heavy, dark-yellow explosive gas, which results from the self-oxidation and reduction of chloric acid, liberated from a chlorate by sulphuric acid:



The solution of this gas in water is yellow and unstable, and contains the hydrate  $\text{ClO}_2 \cdot 8 \text{H}_2\text{O}$ . When dissolved in alkali,  $\text{ClO}_2$  forms chlorite and chlorate thus:—

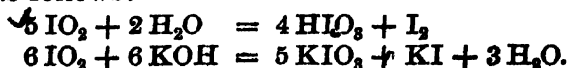


On account of this reaction,  $\text{ClO}_2$  has some claim to be considered the mixed anhydride of chlorous and chloric acids.

**Iodine dioxide**<sup>1</sup> is formed by heating iodic acid with concentrated sulphuric acid until evolution of iodine begins to accompany that of oxygen:



The pure compound is a lemon-yellow solid, decomposing into its elements at  $130^\circ$ . Its reactions with hot water and aqueous alkali are as follows:—



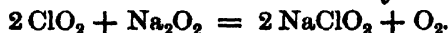
Thus  $\text{IO}_2$  does not appear to resemble  $\text{ClO}_2$  in anhydride character, probably because of the instability or non-existence of iodite.

<sup>1</sup> Muir, *Chem. Soc. Trans.*, 1909, 95, 656

## ACIDS OF THE TYPE HOXO

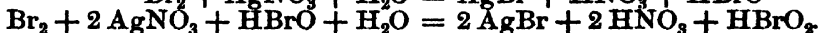
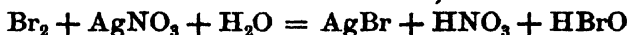
**Chlorous acid**,  $\text{HClO}_2$ , is itself unknown, but some of its salts can be prepared.

Besides being produced in the reaction between chlorine dioxide and sodium hydroxide, sodium chlorite is formed when an aqueous solution of the former is added to sodium peroxide, mutual reduction with evolution of oxygen resulting in the formation in solution of chlorite only:



Several solid chlorites are known, but they are very unstable.

**Bromous acid**,  $\text{HBrO}_2$ , is said to be formed<sup>1</sup> when bromine is added to saturated silver nitrate solution, thus:—



**Acids of the type HOXO<sub>2</sub> (Chloric, Bromic, and Iodic Acids) and their Salts.**—It has already been shown that alkali salts of the type MOX readily pass into the more stable  $[\text{MOXO}_2 + \text{MX}]$  by self-oxidation and reduction thus:—



There does not appear to be much distinction between chlorine and bromine in respect to the above reaction, but in the case of iodine this reaction is much more rapid, taking place even in cold, dilute solution; for not only are the hypoiodites much less stable than the corresponding chlorine and bromine compounds, but the iodates are much more stable than the chlorates or bromates, as the following heats of formation show:—

	Cl	Br	I
H, X, O <sub>3</sub> , Aq.....	239 K	122 K	559 K.

Chlorine has no action on bromic or iodic acid, and these can be obtained by passing chlorine into bromine water, or into iodine suspended in water, the following reaction taking place:—

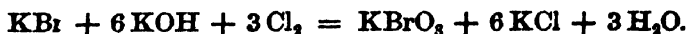


Chloride of bromine or iodine is probably first formed; this then yields hypobromous or hypoiodous and hydrochloric acids by the action of water, the chloranhydrides being thus hydrolysed; the former then give bromic or iodic acid by spontaneous change.

<sup>1</sup> Richards, *J. S. C. I.*, 1906, 25, 4.



Potassium bromate is also formed when chlorine is passed into a warm solution of potassium bromide and hydroxide, thus:—

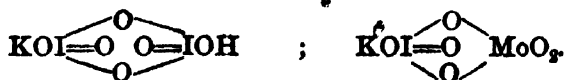


Chlorine, therefore, has no power to decompose potassium bromate.

The superior stability of iodic acid is shown by the fact that iodine displaces chlorine and bromine from chloric and bromic acids respectively, forming iodic acid. (Potassium iodate may be obtained by heating iodine with potassium chlorate.)

The reaction, however, which affords most striking evidence of the difference between iodic acid and the corresponding acids of chlorine and bromine is the direct oxidation of iodine by nitric acid, with production of iodic acid in solution. This acid may be crystallized from its aqueous solution, whilst chloric and bromic acids are known only in such solution; and (when heated to  $170^\circ$  it loses water and leaves iodic anhydride,  $\text{I}_2\text{O}_5$ , as a white, crystalline powder, which is decomposed into its elements at  $300^\circ$ .)

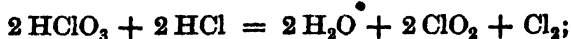
Iodic acid is further distinguished from chloric and bromic acids by the nature of some of its salts; for although the neutral alkali iodates are derivatives of a monobasic meta-acid,  $\text{HIO}_3$ , analogous to chloric and bromic acids, acid salts, such as  $\text{KHI}_2\text{O}_6$ , are known, which exist in solution as true atomic compounds, giving ions  $\text{K}^+$ ,  $\text{HI}_2\text{O}_6^-$ . The free acid must, moreover, be represented by the formula  $\text{H}_2\text{I}_2\text{O}_6$ ; it is a dibasic acid, which, from determination of its electric conductivity, has been shown to be about equal in strength to selenic acid,  $\text{H}_2\text{SeO}_4$ . This acid forms a complex monobasic acid with molybdic anhydride, the analogy of whose potassium salt to potassium di-iodate is shown by the following formulæ:—



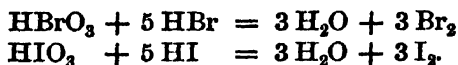
When potassium di-iodate is neutralized in solution by one equivalent of potash, it breaks up into two molecules of  $\text{KIO}_3$ .

**Action of  $\text{HXO}_3$  or  $\text{HX}$  Acids.**—In general this action will involve an oxidation of the hydracid at the expense of the oxygen of the oxyacid. The nature of the reduction product will depend on the existence and stability of the lower oxides or oxyacids of the particular halogen considered.

In the case of chloric acid chlorine dioxide is the reduction product, and the reaction is as follows:—



but with bromic and iodic acids, since no lower oxide exists, the element itself is liberated in each case, thus:—



It is necessary for the free acids to be present, the corresponding alkali salts having no action on one another.

**Acids of the type  $\text{HOXO}_3$ .**—The highest type of halogen oxyacid,  $\text{HOXO}_3$ , in which the halogen is heptavalent, is represented by perchloric and periodic acids and their salts.

Perchloric acid is obtained, together with chlorine and oxygen, when attempts are made to concentrate an aqueous solution of chloric acid; and also when a strong solution of the latter acid is exposed to sunlight. Likewise, when potassium chlorate is carefully heated it may be transformed into perchlorate according to the reaction



although there is generally loss of oxygen according to the reaction

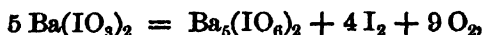


Further, when sulphuric acid acts upon an alkali chlorate perchloric acid results, together with chlorine dioxide. These facts illustrate the superior stability of perchloric acid and the perchlorates, and thus a progressive rise of stability can be traced in the chlorine oxyacids from hypochlorous to perchloric acid. Aqueous solutions of perchloric acid and its salts are so stable as to resist reduction by hydrochloric and sulphurous acids; the anhydrous acid is, however, unstable,

and explodes with violence on contact with oxidisable bodies. It is therefore perchlorate ions which manifest this stability, and not the free acid. The anhydride of this acid,  $\text{Cl}_2\text{O}_7$ , has been obtained by leaving the anhydrous acid in contact with phosphoric oxide kept below  $-10^\circ$ . It is a colourless oil, boiling at  $82^\circ$ , which explodes on percussion.

Perbromic acid and its anhydride have not been obtained. When attempts are made to prepare the acid or its salts, by methods analogous to those which yield perchlorates, a bromide or oxide results, with evolution of oxygen, or bromine and oxygen.

Periodic acid is formed by the action of iodine on an aqueous solution of perchloric acid, and by the electrolytic oxidation of iodic acid. It crystallizes with two molecules of water,  $\text{HIO}_4 \cdot 2\text{H}_2\text{O}$ . Crystallized perchloric acid contains one molecule of water, but this important difference exists between these two hydrates: that whereas only salts of metaperchloric acid exist, so that the molecule of water in the crystalline acid must be regarded simply as water of crystallisation, in the case of periodic acid salts of a pentabasic acid are well known, and therefore the formula must be written  $\text{H}_5\text{IO}_6$ . The barium salt of this acid is obtained by the ignition of barium iodate.



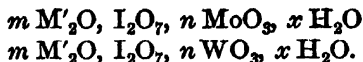
whence the free acid may be obtained in solution by precipitating the barium with the requisite amount of sulphuric acid; the solid acid is, however, unknown, and it is not certain that the anhydride  $\text{I}_2\text{O}_7$  has been obtained. The following stages of hydroxylation of  $\text{I}_2\text{O}_7$  are theoretically possible, and most of them are represented by known salts:—

$\text{I}_2\text{O}_6(\text{OH})_2$	$= 2 \text{IO}_3\text{OH}$ or $\text{HIO}_4$	metaperiodic acid
$\text{I}_2\text{O}_6(\text{OH})_4$	or $\text{H}_4\text{I}_2\text{O}_6$	dimesoperiodic acid
$\text{I}_2\text{O}_4(\text{OH})_6$	$= 2 \text{IO}_2(\text{OH})_3$ or $\text{H}_3\text{IO}_5$	mesoperiodic acid
$\text{I}_2\text{O}_3(\text{OH})_8$	or $\text{H}_5\text{I}_2\text{O}_{11}$	diparaperiodic acid
$\text{I}_2\text{O}_2(\text{OH})_{10}$	$= 2 \text{IO}(\text{OH})_5$ or $\text{H}_5\text{IO}_6$	paraperiodic acid
$\text{I}_2\text{O}(\text{OH})_{12}$	or $\text{H}_{12}\text{I}_2\text{O}_{13}$	—
$\text{I}_2(\text{OH})_{14}$	$= 2 \text{I}(\text{OH})_7$	unknown orthoacid

Derivatives of even more complicated types have been prepared, salts of the hypothetical acids,  $I_4O_9(OH)_{10}$  and  $I_6O_{16}(OH)_{10}$ , being known.

The soluble salts of the polybasic periodic acids suffer hydrolytic dissociation in water, and give an alkaline reaction with litmus. They share this property with other polybasic acids such as phosphoric acid. They may also be considered as basic salts; for instance,  $Na_5IO_6$  may be written  $NaIO_4, 2 Na_2O$ .

Periodic acid and its salts are more stable than their chlorine analogues. The hydroxylation of the anhydride beyond the meta-stage, in the oxyacids of this group, occurs only with periodic acid, though the existence of  $H_2I_2O_6$  shows a doubling of the molecule. Periodic resembles iodic acid in forming complex acids and salts with molybdic and tungstic anhydrides of the general types



**Relative strengths of the halogen oxyacids.**—Little can be said on this subject beyond the statement that acids of the type HOX are exceedingly weak, as indeed appears above, and that the strength of the acids increases with the addition of oxygen. Chloric acid, for instance, is known to be nearly as strong an acid as hydrochloric, and the same relationship is probably true in the case of the oxyacids of bromine and iodine.

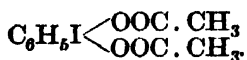
#### CERTAIN OTHER IODINE DERIVATES

Iodine, in distinction from the other halogens, forms several types of organic derivatives in which the element is polyvalent; and these compounds, by virtue of their properties and constitution, suggest analogies between iodine and nitrogen as well as some other elements in the fifth and sixth groups of the periodic system.

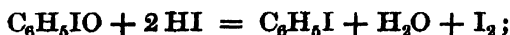
**Iodine trichloride,  $ICl_3$ ,** a yellow crystalline substance, formed by the action of chlorine on the red monochloride, is very unstable, easily decomposing again into  $ICl$  and  $Cl_2$ . It is slowly decomposed by water and alkalis into hydriodic, iodic, hydrochloric, and chloric acids or their salts, so that iodous

acid, of which iodine trichloride is the chloranhydride, and the alkali iodites are unknown.

If an atom of iodine is associated with the phenyl radicle  $C_6H_5$ , the iodobenzene thus resulting, like iodine monochloride, is capable of combining with two atoms of chlorine, forming phenyl iodosochloride,  $C_6H_5ICl_2$ , in which the iodine atom is trivalent; this body is decomposed by dilute aqueous alkali, with the separation of the oxide iodosobenzene,  $C_6H_5I:O$ , whose basic properties are shown by its combination with glacial acetic acid, forming the acetate,



This compound also possesses oxidizing properties, owing to the ease with which its oxygen atom is split off. Iodine, for instance, is liberated by iodosobenzene from hydriodic acid,



and this compound undergoes self-oxidation and reduction when treated with steam, thus:—



The oxidation product is iodobenzene, or iodoxybenzene, which yields up all its oxygen in reaction with hydriodic acid, and also reacts with iodosobenzene and silver oxide in the following manner:—



The product is diphenyliodonium hydroxide, a base which is soluble in water, showing a strongly alkaline reaction, and is thus a derivative of hypothetical iodonium hydroxide,  $IH_2OH$ , which is comparable in type with hydroxylamine,  $NH_2OH$ . The salts of substituted iodonium bases are more nearly related in properties, however, to ammonium compounds.

**Theoretical considerations.**—It will be of interest to inquire how far the existence of these iodonium compounds, which were discovered by Victor Meyer, might be suggested by analogies furnished by the periodic law. It has previously

been shown that the analogues of ammonium in the fifth group are phosphonium, arsonium, and stibonium respectively, only the alkyl derivatives of the two latter basic radicles being known; and that bismuth alkyls, although known, are devoid of basic properties.

Analogues of these compounds exist in the sixth group in the sulphonium derivatives, which are related to hydrogen sulphide as ammonium derivatives are related to ammonia. Since, however, hydrogen sulphide possesses slightly acidic properties, it is only when the hydrogen is replaced by alkyl groups that bases can be formed. Triethylsulphonium hydroxide,  $(C_2H_5)_3SOH$ , is a powerful base which displaces ammonia from its salts. The existence of analogous selenium and tellurium bases is doubtful; tellurium, at least, belongs to the same category in this respect as bismuth.

In the seventh group the two conditions, of comparative electro-positiveness of element and sufficient stability of hydride and its derivatives, are realized only in the case of iodine. Of course hydrogen iodide is no more able to combine with acids to form iodonium salts than hydrogen sulphide to form sulphonium compounds, and, as in the case of arsonium, stibonium, and sulphonium, as well as oxonium derivatives, it is only those in which the hydrogen atoms are replaced by hydrocarbon radicles which exist. The following diagram sets forth these considerations, power to form basic radicles being limited as indicated by the dotted lines *ab* and *cd*—

Gp.VB	Gp.VIB	Gp.VIIB
$XR_4OH$	$XR_3OH$	$XR_2OH$
N	Q	F
P	S	Cl
As	Se	Br
Sb	Te	I
—	—	—
Bi	—	—

Nitrogen, sulphur, and iodine, together with phosphorus, arsenic, and antimony, and to a less extent oxygen as well as perhaps selenium, form the basic radicles under discussion. Fluorine, chlorine, and bromine are too electro-negative to do so; bismuth, and perhaps tellurium, too electro-positive.

Now, although bismuth forms no derivatives of the type  $\text{BiR}_4\text{OH}$ , since its affinity for oxygen increases as that for hydrogen diminishes, it may be expected to form bases in which some of the hydrogen or hydrocarbon residues are replaced by oxygen; and  $\text{Bi}(\text{C}_2\text{H}_5)_2\text{O}$  is a base which forms a nitrate,  $\text{BiC}_2\text{H}_5(\text{NO}_3)_2$ .

Similar compounds of sulphur, selenium, and tellurium exist, and increase in basic properties from sulphur to tellurium. The three following compounds illustrate this principle:—

Diethylsulphoxide  $(\text{C}_2\text{H}_5)_2\text{SO}$ , feebly basic, liberated from its salts by  $\text{BaCO}_3$ ,

Diethylselenoxide  $(\text{C}_2\text{H}_5)_2\text{SeO}$ , a stronger base than the foregoing,

Diethyltelluroxide  $(\text{C}_2\text{H}_5)_2\text{TeO}$ , a strong base, possessing an alkaline reaction, and displacing ammonia from its salts.

Combination with an additional oxygen atom is exemplified in the sixth group by the sulphones, *e.g.* diethylsulphone,  $(\text{C}_2\text{H}_5)_2\text{SO}_2$ . *A priori*, these bodies might be expected either to be basic peroxides, if the second oxygen is feebly attached, or neutral bodies if stable. The sulphones are, in fact, neutral substances which are very stable.

The properties of iodoso and iodobenzene will now be understood in the light of the above remarks.

Iodosobenzene,  $\text{C}_6\text{H}_5\text{IO}$ , is feebly basic, like diethylsulphoxide; and iodobenzene,  $\text{C}_6\text{H}_5\text{IO}_2$ , behaves as a basic peroxide.

The presence of the phenyl rather than the ethyl group in these basic compounds is, however, remarkable, since this radicle generally confers acidic properties, as is shown in the comparison of phenol,  $\text{C}_6\text{H}_5\text{OH}$ , with ethyl alcohol,  $\text{C}_2\text{H}_5\text{OH}$ .

These considerations show, nevertheless, that in the formation of iodonium and allied compounds iodine manifests pro-

perties which might be expected from the position which it occupies in the periodic system.

## MANGANESE

This element is the only known representative of sub-group VII A of the periodic classification, and therefore occupies a unique position. The similarity between manganese and the halogens is very slight, as might be expected from the fact that these elements are members of an extreme group. The resemblance is confined, indeed, to the highest oxide,  $Mn_2O_7$ , and its derivatives, for only when thus combined with the maximum proportion of oxygen does manganese exhibit oxygenic properties at all comparable with those possessed by the halogens. Permanganic acid,  $HMnO_4$ , is thus analogous to perchloric acid,  $HClO_4$ , and potassium permanganate is isomorphous with potassium perchlorate. When, however, these compounds are reduced, so that the type,  $R_2O_7$ , from which they are derived, is departed from, the similarity at once ends; for whilst chlorine maintains its electro-negative character in compounds containing no oxygen, manganese exhibits relationship with its neighbours in the periodic table, chromium and iron, and in its lowest oxidized state yields compounds in which the element is entirely basigenic.

Thus manganates,  $M'_2MnO_4$ , are isomorphous with chromates,  $M'_2CrO_4$ , so that  $MnO_3$  is analogous to  $CrO_3$ ; manganic alum,  $(NH_4)_2SO_4 \cdot Mn_2(SO_4)_3 \cdot 24 H_2O$ , is isomorphous with  $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24 H_2O$ , thus showing an analogy between  $Mn_2O_3$  and  $Fe_2O_3$ ; and, further, certain manganous and ferrous salts form isomorphous double salts with alkali metals, so that  $MnO$  and  $FeO$  are analogous oxides.

With regard to the elements themselves, the contrast between manganese, a hard brilliant metal with a high melting-point, and chlorine, a typical halogen, is very great; whilst the relationship between metallic manganese and chromium and iron is very close.



## SUMMARY OF THE OXIDES OF MANGANESE

**MnO**, a basic oxide yielding manganous salts.

**Mn<sub>2</sub>O<sub>3</sub>**, a very stable neutral oxide: probably a salt.

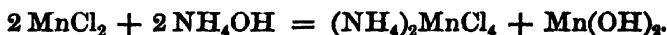
**Mn<sub>2</sub>O<sub>3</sub>**, a feebly basic oxide giving rise to manganic salts.

**MnO<sub>2</sub>**, probably not basic, but possessing feebly acidic properties; may be described as a basic peroxide.

**MnO<sub>2</sub>**, an acidic oxide—manganic anhydride.

**Mn<sub>2</sub>O<sub>7</sub>**, an acidic oxide—permanganic anhydride.

**Manganous oxide, MnO, and its salts.**—MnO is a greyish-green powder which readily oxidizes in air to Mn<sub>3</sub>O<sub>4</sub>; Mn(OH)<sub>2</sub>, a reddish-white precipitate quickly oxidizing to hydrated Mn<sub>2</sub>O<sub>3</sub>. Manganous hydroxide is not quite insoluble in water, and it is only partially precipitated by ammonia on account of the formation of an ammonium double salt which removes manganous ions from the solution:



For the same reason the precipitation of manganous hydroxide by ammonia is completely prevented by the presence of ammonium salts. From such an alkaline solution, however, manganic hydroxide is slowly separated by atmospheric oxidation.

The **manganous salts** are pale pink, their solutions being almost colourless. They are stable in the solid state and in neutral or acid solution, differing in this respect from ferrous salts. The chloride crystallises with 4 H<sub>2</sub>O, the sulphate with 4, 5, or 7 H<sub>2</sub>O, according to temperature. MnSO<sub>4</sub>, 5 H<sub>2</sub>O is isomorphous with CuSO<sub>4</sub>, 5 H<sub>2</sub>O; MnSO<sub>4</sub>, 4 H<sub>2</sub>O, and MnSO<sub>4</sub>, 7 H<sub>2</sub>O with the corresponding hydrates of FeSO<sub>4</sub>. Manganese also forms the double sulphates MnSO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 6 H<sub>2</sub>O, and MnSO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, 6 H<sub>2</sub>O, isomorphous with the corresponding magnesium, zinc, and iron compounds.

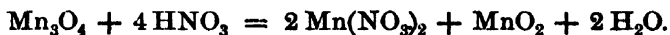
**Mangano-manganic oxide, Mn<sub>3</sub>O<sub>4</sub>**, occurs as a dark-red powder, which is very stable at high temperatures, and is formed when any of the other oxides is ignited in the air.

Mn<sub>3</sub>O<sub>4</sub> is not a simple basic oxide giving rise to a series of salts; its behaviour towards acids shows it to be a compound oxide, whose composition may be either MnO, Mn<sub>2</sub>O<sub>3</sub>, or

$2 \text{MnO}$ ,  $\text{MnO}_2$ . It will be useful to compare this oxide with the apparently analogous oxides  $\text{Pb}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4$ .

There is little doubt that the oxide  $\text{Pb}_3\text{O}_4$  may be considered as  $2 \text{PbO}$ ,  $\text{PbO}_2$ .  $\text{Fe}_3\text{O}_4$ , however, must be considered to be  $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ , since no dioxide in which iron is tetravalent is known to exist. Moreover, a hydrated artificial form of this oxide may be prepared by precipitating a mixture of ferrous and ferric salts with caustic alkali.\*

In the case of  $\text{Mn}_3\text{O}_4$ , therefore, a correct view of its constitution depends upon the nature of the oxide  $\text{Mn}_2\text{O}_3$ . This will be discussed below; meanwhile the following reactions of  $\text{Mn}_3\text{O}_4$  may be stated. This oxide dissolves slowly in cold concentrated sulphuric acid, forming a red solution which contains both manganous and manganic sulphates. So far the constitution,  $\text{MnO}$ ,  $\text{Mn}_2\text{O}_3$ , is upheld. On heating, however, with dilute sulphuric acid or with nitric acid, manganous salt and  $\text{MnO}_2$  are formed:



This reaction supports the constitution,  $2 \text{MnO}$ ,  $\text{MnO}_2$ .

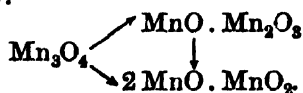
✓ **Manganic oxide**,  $\text{Mn}_2\text{O}_3$ , may be obtained as a black powder by heating the other oxides in a current of oxygen. The corresponding hydroxide,  $\text{MnO} \cdot \text{OH}$ , is formed when manganous hydroxide oxidizes in the air, and also when manganic sulphate is decomposed by water. The behaviour of this oxide or hydroxide towards acids is significant. The hydroxide dissolves in cold hydrochloric acid, forming a dark-brown solution, which evolves chlorine when heated. In all probability this solution contains  $\text{MnCl}_3$ . Neither the oxide nor hydroxide dissolves to any extent in cold sulphuric acid. Hot strong nitric acid, however, dissolves the hydroxide, forming manganous nitrate and precipitating the dioxide:



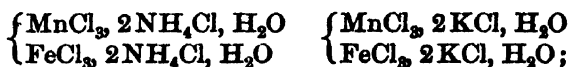
**Manganic salts** are very unstable, and are decomposed by water. **Manganic potassium alum** separates in violet octahedra on crystallizing the solution obtained from  $\text{Mn}_3\text{O}_4$  and strong sulphuric acid, after the addition of potassium sulphate. It

is decomposed by water, with the precipitation of manganic hydroxide.

These facts point to the conclusion that manganic oxide and hydroxide possess basic functions and a constitution corresponding thereto, but that on heating with acids a separation takes place into  $\text{MnO}$ , which dissolves, and  $\text{MnO}_2$ , which is precipitated. The constitution of  $\text{Mn}_3\text{O}_4$  and the reactions involving the separation of  $\text{MnO}_2$  may be represented in accordance with this view as follows:—



The combination of  $\text{Mn}_2\text{O}_3$  with  $\text{MnO}$  suggests the possession of feebly acidic properties by the former oxide. Similarly, manganic chloride,  $\text{MnCl}_3$ , should possess some of the properties of a chloranhydride. This is shown probably to be the case by the solubility of this compound in ether and absolute alcohol, and more particularly by its combination with alkali chlorides (to form, *e.g.*  $\text{K}_2\text{MnCl}_5$ ), and the hydrochlorides of certain organic bases to form compounds of the type  $\text{MnCl}_3 \cdot 2\text{RHCl}$ . The isomorphism of the following pairs of compounds bears out the analogy between Mn and Fe:—

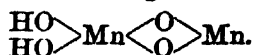


though ferric salts are much more stable than manganic salts.

**Manganese dioxide or peroxide,  $\text{MnO}_2$ .**—This oxide, well known on account of its use in the manufacture of chlorine, is of a dark-brown or black colour.

Precipitated hydrated manganese dioxide, obtained by adding alkaline hypochlorite to the solution of a manganous salt, just as  $\text{PbO}_2$  is obtained from a lead salt, easily passes into the colloidal state, producing a brown liquid, which is acid in reaction. Such a liquid appears to contain manganous acid,  $\text{H}_2\text{MnO}_3$ , or  $\text{H}_4\text{MnO}_4$ . A similar solution is produced<sup>o</sup> transitorily in the titration of hot acidified oxalic-acid solution with permanganate. Various compounds of  $\text{MnO}_2$  with

basic oxides are known.  $K_2Mn_5O_{11}$  is a yellow powder, and  $CaMn_5O_{11}$  is a dark-brown precipitate formed by pouring manganous-nitrate solution into excess of bleaching-powder solution. The manganese mud formed by the oxidation of manganous hydroxide in the presence of lime in the Weldon recovery process contains a calcium manganite; and the hydrated  $Mn_2O_3$ , produced by atmospheric oxidation of  $Mn(OH)_2$ , may be regarded as manganous manganite:

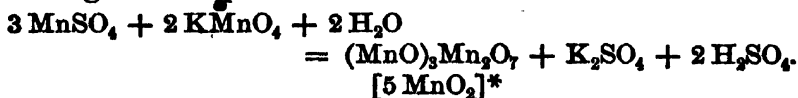


It will thus be concluded that manganese dioxide possesses the properties of feebly acidic anhydride. It is probably not a basic oxide, since it forms no oxysalts. **Manganese tetrachloride**,  $MnCl_4$ , has, however, been obtained by the action of dry hydrogen chloride on manganese dioxide suspended in carbon tetrachloride. It is unstable, but forms complex salts, such as  $K_2MnCl_6$ .

Manganese dioxide is not a superoxide in the sense of yielding hydrogen peroxide with acids, and it is questionable whether this compound can be represented as a simple polyoxide having the constitution  $O=Mn=O$ . Reactions are known which appear to indicate the saline nature of this compound; for instance, the dioxide is precipitated, apparently as manganous manganate, when barium manganate and manganous sulphate interact:



and is also formed by the action of potassium permanganate on manganous sulphate solution:



The above reactions may, however, be regarded more simply as instances of oxidation of manganous salt with the corre-

\* A seeming analogy to this reaction is furnished by the following:—

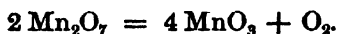


chromium dioxide, however, is an unstable salt, decomposed by water into chromic acid and chromic oxide.

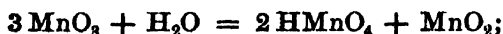
sponding reduction of manganate or permanganate to the dioxide stage. In any case the molecular constitution of manganese dioxide must remain undecided.

**Manganese trioxide—Manganic anhydride,  $\text{MnO}_3$ .**—This oxide, the anhydride of manganic acid, is unstable, and can only be obtained in small quantity. It is evolved as a pink fume, which may be condensed to a red, viscid solid, when a solution of potassium permanganate in concentrated sulphuric acid is dropped on to dry sodium carbonate.

The  $\text{MnO}_3$  owes its existence to the spontaneous decomposition of permanganic anhydride,  $\text{Mn}_2\text{O}_7$ , as follows:—

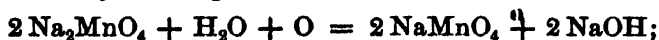


Manganic anhydride is decomposed by water in the following manner:—



from which it may be concluded that manganic acid is an unstable substance.

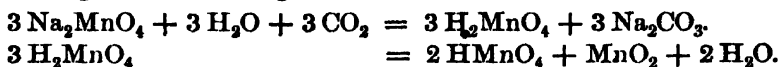
**The manganates.**—The instability of the acid is shared by its salts, the manganates. Sodium manganate is a green substance formed by heating together manganese dioxide and caustic soda in air or with an oxidising agent. It may be obtained in small crystals, having the composition  $\text{Na}_2\text{MnO}_4$ ,  $10 \text{H}_2\text{O}$ , which are isomorphous with Glauber's salt. Thus an analogy between manganese and the members of the sixth family is established. The alkali manganates pass into permanganates by atmospheric oxidation thus:—



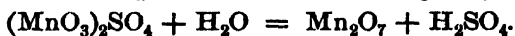
and since manganic acid itself, if formed, would decompose spontaneously into permanganic acid and manganese dioxide, as may be concluded from the action of water on its anhydride, any reaction which liberates this acid, will cause such decomposition to take place.

Now when sodium manganate is dissolved in a little water a deep-green solution is obtained, which, on dilution with much water, or the addition of a little acid, turns pink, owing

to the formation of permanganate. It is doubtful whether pure water can effect this change, but, in the absence of other acid, carbonic acid derived from the air promotes it. The change is due to the hydrolysis of the manganate, and the self-oxidation and reduction of the resulting manganic acid according to the following reactions:—



**Manganese heptoxide**—**Permanganic anhydride**,  $\text{Mn}_2\text{O}_7$ .—Potassium permanganate dissolves in concentrated sulphuric acid, forming a green liquid. It is apparent from this change of colour that a chemical change has taken place, and it is believed that the solution contains the sulphate  $(\text{MnO}_3)_2\text{SO}_4$ . If a little water is added to this solution while it is kept cool, a dark reddish-brown liquid separates, which does not solidify at  $-20^\circ$ . This is permanganic anhydride, formed by the decomposition of the sulphate in the following way:—



It is very unstable, easily decomposing into a lower oxide and oxygen, the evolved oxygen carrying with it violet fumes of the anhydride. It dissolves in water, forming a violet solution of permanganic acid, and in strong sulphuric acid, with the regeneration of the above green sulphate. The existence of this compound recalls that of the uranyl salts, which are derived from uranic oxide,  $\text{UO}_3$ , by the replacement of 1 atom of oxygen by acidic radicles.

**Permanganic Acid**,  $\text{HMnO}_4$ , and the **Permanganates**.—The solution obtained by decomposing barium permanganate with its equivalent of dilute sulphuric acid yields on slow evaporation violet-black crystals of permanganic acid, which are very unstable, easily decomposing into manganese dioxide, oxygen, and water.

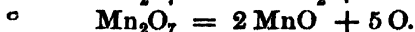
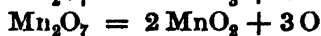
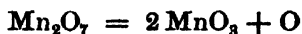
**Permanganic chloride**,  $\text{MnO}_3\text{Cl}$ , is known; and, both as regards its manner of preparation, by the action of hydrogen chloride on  $(\text{MnO}_3)_2\text{SO}_4$ , and its properties, including its reduction with water, it is shown to be a true acid chloride.

**Potassium permanganate** is the most important salt of permanganic acid. It is usually prepared by heating together caustic potash, potassium chlorate, and manganese dioxide, extracting with water, and passing  $\text{CO}_2$  through the liquid to convert manganate into permanganate. The crystals of this salt consist of almost black rhombic prisms, with a green metallic lustre, which are isomorphous with potassium perchlorate. They yield a red powder, and dissolve in water, forming a deep-purple solution. This solution slowly decomposes in presence of traces of organic matter with separation of manganese dioxide. When solid  $\text{KMnO}_4$  is heated to  $240^\circ$  it decomposes as follows:—



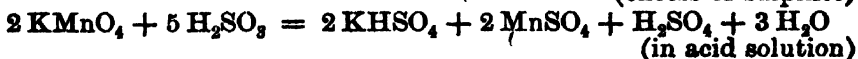
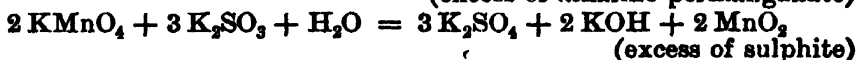
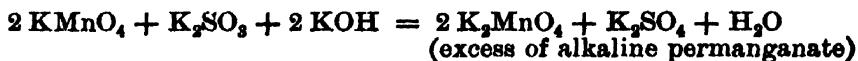
With concentrated sulphuric acid permanganic acid is first separated, permanganic sulphate also being formed, and this breaks up on heating into manganese dioxide, oxygen, and water, manganous sulphate eventually resulting.

Potassium permanganate is a valuable oxidizing agent. Three stages in its reduction may be observed, the decomposition products being respectively potassium manganate, manganese dioxide, and a manganous salt. These changes may thus be represented in terms of oxides:—



The first reaction takes place in alkaline, the second in alkaline or neutral solution, the last generally<sup>1</sup> in presence of free acid.

The following examples with sulphites are typical<sup>2</sup>:—



<sup>1</sup> An interesting example of reduction to the  $\text{MnO}$  stage in alkaline solution is furnished by adding a very little dilute permanganate to sulphite solution containing ammonia and much ammonium chloride. A colourless liquid results on boiling which probably contains ammonium manganous chloride.

<sup>2</sup> See chap iv for a further discussion of the reactions of permanganate.

Other permanganates are similar to the potassium salt, that of silver being the least soluble in water.

Permanganic acid is a strong acid, comparable with perchloric acid. Its salts are largely dissociated in aqueous solution, and give an absorption spectrum characteristic of the permanganate ion.

## CHAPTER XII

### GROUP VIII

The members of this group occupy a unique position in the periodic table. In each of the three long periods of seventeen elements, the two sets of seven analogues to the elements of the short or typical periods are linked by sets of three, which constitute transitional elements, and are classed together as Group VIII. There are thus nine members of the group, which are related in the following manner to the adjacent sub-groups:—

A					B	
vi	vii	viii			i	ii
Cr	Mn	Fe	Co	Ni	Cu	Zn
Mo	—	Ru	Rh	Pd	Ag	Cd
—	—	—	—	—	—	—
W	—	Os	Ir	Pt	Au	Hg

The eighth group is thus peculiar in the possession of three members in each series instead of only one; and it would appear that the variation of atomic weights and properties from group to group would on this account be destroyed. Such, however, is not the case, owing to the remarkable fact that the three members in each series have approximately equal atomic weights and physical properties, so that they are analogous to a single element in any other group.

	Fe	Co	Ni	Ru	Rh	Pd	Os	Ir	Pt
Atomic weight	55·85	58·97	58·68	101·7	102·9	106·7	190·9	193·1	195·2
Density .....	7·84	8·8	8·9	12·06	12·1	11·4	22·48	22·42	21·42
Atomic volume	7·12	6·70	6·59	8·43	8·50	9·36	8·49	8·60	9·11



The melting-points of these elements are high, that of nickel, about  $1484^{\circ}$ , being the lowest, and those of rhodium, iridium, and osmium the highest. Iron, with melting-point about  $1600^{\circ}$ , and platinum, with melting-point about  $1750^{\circ}$ , have been vaporized in the electric furnace at a temperature of upwards of  $3000^{\circ}$ .

The densities of the members of the different sets are related to one another in an approximately similar manner to the atomic weights; so that ruthenium, rhodium, and palladium are intermediate in density as well as in atomic weight between iron, cobalt, and nickel, and the very heavy metals, osmium, iridium, and platinum. With rise of atomic weight there is a diminution of electro-positiveness, as indicated by the potential series; and concomitant with this is a diminution in chemical activity, in passing, for example, from nickel through palladium to platinum; this being illustrated by the mode of natural occurrence and relative ease of reduction of the metals of the group. Iron seldom occurs, and cobalt and nickel never occur, native, though their oxides are easily reduced; but osmium, iridium, and platinum are always found in the free state.

The mutual relationships of the metals of the eighth group recall those obtaining between copper, silver, and gold in group IB, to which metals they show much resemblance.

Manifestly the members of this group cannot be divided into A and B sub-groups as in the case of other groups; but they may be conveniently studied in the sets into which they naturally fall by reason of their atomic weights and physical properties.

Since the maximum valency of the members of this family is eight, it is to be expected that these metals will show a large variety of types of compound, as in the case of manganese, in which different valencies from two to seven are manifested. This expectation is realized to some extent in the case of iron, though less with cobalt and nickel. The higher members of the eighth group possess chemical properties which ally them to gold, to which they approximate in the periodic

system. Fairly complete series of oxides and halides are known, acidic being in most cases more prominent than basic properties.

### IRON, COBALT, AND NICKEL

In physical properties cobalt and nickel stand much nearer to one another than they do to iron. This is also true of their chemical relationships, so that in some respects iron stands alone among the elements. Moreover, iron shows a strong likeness to manganese, its neighbour in the seventh group, as well as to chromium. Iron is strongly magnetic, cobalt and nickel feebly so. All three metals possess high melting-points. Whilst iron rusts in moist air, cobalt and nickel are only oxidized when heated in the air. Red-hot iron decomposes steam, with formation of the oxide  $\text{Fe}_3\text{O}_4$ . Cobalt and nickel form the monoxides under similar circumstances. These three metals enter into various complex radicles, forming a number of complicated compounds, such as the double cyanides and metallic ammines, but nickel shows less tendency to form these compounds than iron and cobalt. In this and other respects nickel approximates to copper, whilst cobalt is more nearly related to iron. It must be observed, therefore, that according to properties, the order of these elements in the group is Fe, Co, Ni—although the atomic weight of cobalt is distinctly greater than that of nickel.

#### OXIDES OF THE TYPE MO AND THEIR SALTS

Each of these metals forms a monoxide which is basic.

**Ferrous oxide**,  $\text{FeO}$ , is a black powder, whose white hydroxide,  $\text{Fe}(\text{OH})_2$ , is precipitated by alkali from a ferrous solution in absence of air. When a little air is present, a dark-coloured compound of  $\text{Fe}(\text{OH})_2$  and  $\text{Fe}(\text{OH})_3$  is produced, which turns to rust-coloured  $\text{Fe}(\text{OH})_3$  on further exposure. The precipitation of  $\text{Fe}(\text{OH})_2$  by ammonia is completely prevented by sufficient ammonium chloride. Ferrous compounds are not so oxidisable as the otherwise analogous chromous compounds.

**Ferrous salts** are white when anhydrous, and pale-green or bluish when hydrated. The most important is **ferrous sulphate** or green vitriol,  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ . In the heptahydrated condition this salt is isomorphous with magnesium and zinc sulphates; crystals having the composition  $\text{FeSO}_4 \cdot 5 \text{H}_2\text{O}$  have also been obtained which are isomorphous with  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ , and also a salt  $\text{FeSO}_4 \cdot 4 \text{H}_2\text{O}$  isomorphous with  $\text{MnSO}_4 \cdot 4 \text{H}_2\text{O}$ .

**Ferrous ammonium sulphate**,  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6 \text{H}_2\text{O}$ , is isomorphous with the corresponding magnesium, zinc, and manganous double salts. The chemical union between ferrous sulphate and ammonium sulphate is sufficient to protect the iron to a certain extent from atmospheric oxidation, so that this salt is much more stable than ferrous sulphate.

**Cobaltous oxide**,  $\text{CoO}$ , is a brown powder, and the hydroxide is rose red, although a blue basic salt is first obtained when the solution of a cobaltous salt is precipitated by alkali hydroxide. The hydroxide is oxidised by exposure to air, hydrated  $\text{Co}_3\text{O}_4$  being produced. It is soluble in hot strong potassium-hydroxide solution, though it can hardly be said to combine with the base, since it crystallises from the solution on cooling. **Cobaltous salts** are blue, green, or violet when anhydrous, and red or crimson when hydrated. The sulphate is heptahydrated, isomorphous with ferrous and other sulphates, and forms similar double salts.

**Nickelous oxide**,  $\text{NiO}$ , is a green crystalline powder obtained from the hydroxide by ignition. When heated at a moderate temperature in air it is converted into the sesquioxide,  $\text{Ni}_2\text{O}_3$ , but loses oxygen on further heating, leaving the monoxide, which is stable even at the temperature of the electric furnace. The hydroxide is a green precipitate which, unlike ferrous hydroxide, does not oxidise in air. The **nickelous salts** are usually yellow when anhydrous, and bright green when hydrated. The sulphate generally crystallizes with seven molecules of water, and is isomorphous with ferrous and other sulphates. The double sulphate,  $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6 \text{H}_2\text{O}$ , is isomorphous with analogous salts containing magnesium zinc, manganese iron, or cobalt.

OXIDES OF THE TYPE  $M_2O_3$ 

$Fe_3O_4$  and  $Co_3O_4$  are well known, but the existence of  $Ni_3O_4$  is doubtful.  $Fe_3O_4$ , magnetic oxide of iron, is **ferrosoferric oxide**, that is, a compound of ferrous and ferric oxides,  $FeO$ ,  $Fe_2O_3$ . It is black, magnetic, and very stable, since it is obtained by passing steam over red-hot iron, and is the oxide formed when iron is heated in air or oxygen. It may be prepared artificially in a hydrated state by mixing ferrous and ferric solutions in the right proportions and precipitating the mixture with alkali hydroxide. It is not a basic oxide forming salts, but a compound oxide, which may itself be a salt (*cf.*  $Pb_3O_4$  and  $Mn_3O_4$ ).

**Cobaltocobaltic oxide**,  $Co_3O_4$ , is obtained by heating cobaltous oxide or nitrate in the air, or in a hydrated condition by the oxidation of moist cobaltous hydroxide; it is analogous to magnetic oxide of iron, and probably has the same constitution.

OXIDES OF THE TYPE  $M_2O_3$  AND THEIR SALTS

✓ **Ferric oxide**,  $Fe_2O_3$ , is a dark-red powder, which may be obtained by igniting the hydroxide  $Fe(OH)_3$ . ✓ **Ferric hydroxide** is formed as a brown precipitate when ammonia is added in excess to a cold solution of a ferric salt. When this precipitate is heated it passes through several stages of dehydration until the anhydrous oxide remains. It is possible for ferric hydroxide to exist in a colloidal condition; this is produced by dissolving ferric hydroxide in ferric-chloride solution, or by adding ammonia to ferric chloride as long as the precipitate can be redissolved, and then submitting the liquid to dialysis. The ferric chloride molecules pass through the membrane, leaving almost pure ferric hydroxide in colloidal suspension.

Ferric oxide is a basic oxide, giving rise to the ferric salts, of which the chloride is the best known.

✓ **Ferric chloride**,  $FeCl_3$ , occurs in almost black crystalline plates, which are deliquescent and soluble in water, as well as in alcohol, ether, and other organic solvents. It crystallizes

from aqueous solution in yellow masses of the composition  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , and occurs in other hydrated forms. The anhydrous salt begins to volatilize even at  $100^\circ$ , and its vapour density at low temperatures almost corresponds to the formula  $\text{Fe}_2\text{Cl}_6$ . As the temperature rises the vapour density diminishes. This appears to be due partly to dissociation into molecules of  $\text{FeCl}_3$ , and partly to decomposition into ferrous chloride and chlorine.

The molecular weight of ferric chloride in organic solvents corresponds to the formula  $\text{FeCl}_3$ . This salt is slowly but completely hydrolysed by water into colloidal ferric hydroxide and hydrochloric acid. This fact, together with the solubility in organic solvents, shows ferric chloride to possess some of the properties of a chloranhydride, as well as of a salt. The existence of various double salts, such as  $\text{FeCl}_3 \cdot \text{MgCl}_2 \cdot \text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ , further illustrates this fact.

✓ **Ferric sulphate**,  $\text{Fe}_2(\text{SO}_4)_3$ , is a white powder which is easily decomposed, forming basic salts, and is completely hydrolysed by excess of boiling water. It forms double salts with the sulphates of the alkalis, the well-known iron alums, isomorphous with the similarly constituted aluminium, chromium, and manganese alums. **Ammonium iron alum**,  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , forms light violet crystals which dissolve in water, giving a brown solution, this colour being due to the formation of basic ferric sulphate by hydrolysis.

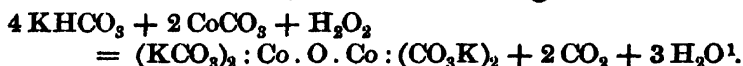
Besides its basic function ferric oxide possesses feebly acidic properties, as indeed would be gathered from the properties of the salts. Ferric oxide combines at high temperatures with certain basic oxides to form ferrites, which are definite, well-crystallized compounds. The best known are calcium ferrite,  $\text{CaFe}_2\text{O}_4$ , magnesium ferrite,  $\text{MgFe}_2\text{O}_4$ , and zinc ferrite,  $\text{ZnFe}_2\text{O}_4$ . Magnetic oxide of iron is ferrous ferrite,  $\text{FeFe}_2\text{O}_4$ . In this property ferric oxide resembles alumina, though its acidic functions are much less pronounced, as is shown by the fact that ferric hydroxide is insoluble in potassium hydroxide, while aluminium hydroxide is soluble.

✓ **Cobaltic oxide**,  $\text{Co}_2\text{O}_3$ . Cobaltous compounds are more easily

oxidised than the corresponding nickelous compounds. It has been seen that cobaltous hydroxide is oxidised by air, whilst nickelous hydroxide is stable in air. Ammoniacal cobaltous solutions readily absorb oxygen, forming the cobaltic ammines, a series of complicated compounds which will be studied later. Cobaltic hydroxide is precipitated by means of hypochlorite solution more easily than the corresponding nickelic compound. Cobaltous salts generally result when cobaltic oxide is dissolved in acids, but cobaltic acetate is thus produced.

✓ **Cobaltic sulphate**,  $\text{Co}_2(\text{SO}_4)_3$ , may be prepared by the electrolytic oxidation of an acidified solution of the cobaltous salt. It forms blue crystals with  $18 \text{H}_2\text{O}$  and is unstable. From it **ammonium cobaltic alum** can be obtained by adding the requisite quantity of ammonium sulphate and crystallising. This salt forms blue octahedra, which decompose in contact with water, evolving ozonised oxygen.

When a little cobaltous solution is added to a solution of potassium bicarbonate containing hydrogen peroxide, a bright green liquid results which probably contains a complex **potassium cobaltic carbonate**, formed according to the reaction:



**Nickelic oxide**,  $\text{Ni}_2\text{O}_3$ , is obtained by the gentle ignition of nickelous nitrate or carbonate in the air. It is also gradually precipitated in a hydrated state from the solution of a nickelous salt by alkali hypochlorite<sup>2</sup>. It is not a basic oxide, but dissolves in acids with the evolution of oxygen or its equivalent. It is therefore a **basic peroxide**, like manganese dioxide, and on strong ignition loses oxygen, leaving  $\text{NiO}$ .

#### OXIDES OF THE TYPE $\text{MO}_2$

Iron forms no compounds of the type  $\text{MO}_2$ , but definite crystalline nickelites and cobaltites, decomposable by water, such as  $\text{BaO}, 2\text{NiO}_2$ ,  $\text{BaO}, \text{CoO}_2$ ,  $\text{BaO}, 2\text{CoO}_2$ ,  $\text{MgO}, \text{CoO}_2$ , are

<sup>1</sup> Durrant, *Chem. Soc. Trans.*, 87, 1905, 1781.

<sup>2</sup> According to Bellucci and Clavari (*Gazzetta*, 1905, 14, II, 234), however, this precipitate is  $\text{NiO}_2$ ,  $\approx \text{H}_2\text{O}$ .

formed by heating the sesquioxides with suitable basic oxides at high temperatures.

#### THE TYPE $\text{MO}_3$

This type, which is so characteristic of the sixth group, is represented amongst the three metals at present under consideration by the salts of ferric acid,  $\text{H}_2\text{FeO}_4$ , though neither the acid nor its anhydride,  $\text{FeO}_3$ , is known. **Potassium ferrate**,  $\text{K}_2\text{FeO}_4$ , existing in dark red crystals, isomorphous with potassium chromate and sulphate, and forming a purple solution, is produced by heating together powdered iron, potassium hydroxide, and nitrate, by passing chlorine into a strong potash solution in which ferric hydroxide is suspended, or by the electrolytic oxidation of iron in a similar solution. The salt is unstable, its solution easily breaking up as follows:—



The barium salt is more stable, and may be dissolved in dilute acetic acid without decomposition.

#### THE PLATINUM METALS

The six metals, **ruthenium**, **rhodium**, **palladium**, **osmium**, **iridium**, and **platinum**, which are associated together in nature, are allied to one another by physical and chemical properties. They are greyish white, very infusible, and show little reactivity, being therefore easily liberated from their compounds. This latter property accounts for their being found in nature in the free state, and is connected with the small atomic volumes of the metals themselves, as has been previously shown. They fall into two groups, with approximately equal atomic weights:

ruthenium, rhodium, palladium;  
osmium, iridium, platinum;

and, moreover, the pairs, ruthenium and osmium, rhodium and iridium, palladium and platinum, present natural relationships in properties. For instance, palladium and platinum both oc-

## COMPOUNDS OF THE PLATINUM METALS

Typical Oxides	Ru	Rh	Pd	Os	Ir	Pt
MO.....	— RuCl <sub>3</sub> (?)	RhO	PdO { PdCl <sub>2</sub> , PdSO <sub>4</sub> , K <sub>2</sub> PdCl <sub>4</sub> }	OsO OsCl <sub>2</sub>	— IrCl <sub>3</sub>	PtO PtCl <sub>2</sub> , K <sub>2</sub> PtCl <sub>6</sub>
M <sub>2</sub> O.....	—	—	—	—	—	Pt <sub>2</sub> O <sub>4</sub> (?)
M <sub>2</sub> O <sub>3</sub> .....	Ru <sub>2</sub> O <sub>3</sub> RuCl <sub>3</sub> , K <sub>2</sub> RuCl <sub>6</sub>	Rh <sub>2</sub> O <sub>3</sub> , RhCl <sub>3</sub> , K <sub>2</sub> RhCl <sub>6</sub> , Na <sub>2</sub> RhCl <sub>6</sub> , Rh <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> , and alums	—	Os <sub>2</sub> O <sub>3</sub> OsCl <sub>3</sub> , K <sub>2</sub> OsCl <sub>6</sub>	Ir <sub>2</sub> O <sub>3</sub> { IrCl <sub>3</sub> , K <sub>2</sub> IrCl <sub>6</sub> , Ir <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> , and alums }	—
MO <sub>2</sub> .....	RuO <sub>2</sub> (RuCl <sub>4</sub> ), K <sub>2</sub> RuCl <sub>6</sub> , Ru(SO <sub>4</sub> ) <sub>2</sub>	RhO <sub>2</sub>	PdO <sub>2</sub> PdCl <sub>4</sub> , K <sub>2</sub> PdCl <sub>6</sub>	OsO <sub>2</sub> OsCl <sub>4</sub> , K <sub>2</sub> OsCl <sub>6</sub>	IrO <sub>2</sub> { IrCl <sub>4</sub> , K <sub>2</sub> IrCl <sub>6</sub> , Ir(SO <sub>4</sub> ) <sub>2</sub> }	PtO <sub>2</sub> PtCl <sub>4</sub> , K <sub>2</sub> PtCl <sub>6</sub> , Pt(SO <sub>4</sub> ) <sub>2</sub>
MO <sub>3</sub> .....	(RuO <sub>3</sub> ), K <sub>2</sub> RuO <sub>4</sub>	—	—	(OsO <sub>3</sub> ), K <sub>2</sub> OsO <sub>4</sub>	—	K <sub>2</sub> O, 3PtO <sub>3</sub>
M <sub>2</sub> O <sub>4</sub> .....	(Ru <sub>2</sub> O <sub>7</sub> ), KRuO <sub>4</sub>	—	—	—	—	—
MO <sub>4</sub> .....	RuO <sub>4</sub>	—	—	OsO <sub>4</sub>	—	—

Compounds in round brackets ( ) are unknown, but their derivatives exist.



clude hydrogen, and also form compounds of the type  $K_2MCl_4$ ; and ruthenium and osmium are alone in forming derivatives of the type  $MO_3$  and the tetroxides  $MO_4$ . In their chemical properties the members of the group show intermediate rather than extreme characters, since their various oxides present prominently neither basic nor acidic qualities. This is quite in accord with their position in the periodic table, between chromium, molybdenum, and tungsten on the one hand, and zinc, cadmium, and mercury on the other. They likewise exhibit some relationships to the members of the iron group, which are manifested chiefly in the complex cyanides and ammines.

The table on p. 319 includes representatives of most of the simple compounds of the platinum metals. Although halides corresponding to several types are well known, comparatively few oxy-salts appear to exist. This shows that the basic functions of the oxides of these metals are very feebly developed.

**The oxides of the type  $MO$**  are dark-coloured powders, insoluble in water and most acids. They may be prepared by ignition of the metal in air or oxygen, or by heating the corresponding halide with sodium carbonate. They are decomposed again into their elements by stronger ignition. The hydroxides may sometimes be obtained by decomposing the dichlorides with hot caustic alkali. **Platinous hydroxide**, for instance, may be prepared in this way. It is difficult, however, to obtain the compound pure, as the chloride is only slowly decomposed, and the hydroxide also shows a tendency to combine with excess of the base. When obtained pure by the action of the theoretical amount of alkali hydroxide on potassium chloroplatinite,  $K_2PtCl_4$ , in dilute solution, platinous hydroxide is found to be soluble in hydrochloric and hydrobromic acids, and also in sulphurous acid, but not in other oxyacids. Moreover, it is decomposed by boiling alkali-hydroxide solution into metal and dioxide.

**Halides of the type  $MX_2$**  exist in the case of most of the metals, but they do not present truly saline characters. It will be judged from these facts that there are but slight grounds for

considering oxides of the type  $MO$  to be basic oxides. Indeed acidic functions appear in the tendency to combine with alkalis; and this is further illustrated in the case of the dichlorides of palladium and platinum by the formation of **chloropalladites** and **chloroplatinites** (or **platinochlorides**); *e.g.*  $K_2PdCl_4$  and  $K_2PtCl_4$  respectively.

The oxides of the type  $M_2O_3$ , and their derivatives, are of little importance. The oxides show less tendency to combine with acids than the monoxides previously considered. **Rhodic nitrate**,  $Rh(NO_3)_3$ , and **sulphate**,  $Rh_2(SO_4)_3$ , are known, the latter forming a series of alums with the alkali sulphates. The complex chlorides  $K_3OsCl_6$  and  $K_3IrCl_6$  illustrate the acidic functions of the type.

The oxides of the type  $MO_2$ , and their derivatives, are the most important compounds of the group. The dioxides of all the six metals are known, and are for the most part stable bodies which are prepared from other compounds by ignition. The corresponding hydroxides, which may be prepared by decomposing the tetrachlorides with alkali hydroxide, possess feebly basic properties; and the sulphates  $Ru(SO_4)_2$ ,  $Ir(SO_4)_2$ , and  $Pt(SO_4)_2$  are known. Moreover, certain of the dioxides form definite compounds with alkalis. **Sodium platinate**,  $Na_2O, 3PtO_2, 6H_2O$ , for instance, has been obtained in a crystalline condition. Likewise the tetrachlorides combine with the chlorides of the alkali metals to form well-known complex salts containing the acidic ion " $(MCl_6)$ ". The best-known of these salts are the **chloroplatinates** or **platinichlorides**; for instance,  $K_2PtCl_6$ .

The type  $MO_3$  is represented by compounds of ruthenium and osmium only. Ruthenium forms a salt, **potassium ruthenate**,  $K_2RuO_4$ , corresponding to the unknown anhydride  $RuO_3$ ; this salt, by its mode of preparation and properties, calls to mind potassium manganate, for it is converted by dilute acids into **potassium perruthenate**,  $KRuO_4$ , with separation of a precipitate of a lower oxide. The perruthenate is also formed by the action of chlorine on a solution of the ruthenate. **Potassium osmate**,  $K_2OsO_4, 2H_2O$ , crystallizes in octahedra.

The tetroxides  $\text{RuO}_4$  and  $\text{OsO}_4$  are the only known compounds in which four atoms of oxygen are united to a single atom of another element. The nearest approach to this high state of oxidation is seen in permanganic and perchloric anhydrides. Now the acid corresponding to  $\text{Mn}_2\text{O}_7$ , viz., permanganic acid, although unstable, is a powerful acid, judging by the extent of its electrolytic dissociation in aqueous solution; and this is in accordance with the generally observed fact that the presence of oxygen intensifies acidity.

In the case of ruthenium, salts corresponding to the acids  $\text{H}_2\text{RuO}_4$  and  $\text{HRuO}_4$  are known, as was mentioned above, although the acids themselves have never been obtained. Since the tetroxide dissolves in water it would be expected to form a strong acid. This, however, is not the case, for the solution does not possess an acid reaction, and does not decompose carbonates or form crystalline salts. The same is true of the corresponding solution of osmium tetroxide, which is erroneously known as osmic acid. Both these oxides are low-melting, volatile solids, which, when heated, decompose into oxygen and the dioxide. Their solutions are reduced by organic matter with the precipitation of finely-divided metal. On this account a solution of "osmic acid" is used for staining microscopic preparations.

The neutral property of these tetroxides, due to complete absence of hydroxylation in aqueous solution, presents a unique phenomenon. It has been previously observed, however (p. 46), that power of hydroxylation of typical oxides diminishes regularly from the fourth group onwards, and consequently should disappear in the eighth group. There are no analogues of ruthenium and osmium in sub-group VII A, the only known member of this sub-group being manganese; but permanganic acid is strictly monobasic. Therefore the neutral character of these tetroxides is quite in accordance with the requirements of the periodic law, and at the same time illustrates well the generally inert character of the oxides of the eighth group.

## COMPLEX CYANIDES, AMMINES, AND ALLIED COMPOUNDS

Two important classes of compounds formed by members of the eighth group remain to be considered; namely, the **complex cyanides** and the **ammines**, or ammoniacal bases. Each of these classes of compound is characteristic of the eighth group as a whole, as well as of some of its immediate neighbours in the periodic table. They will therefore be studied from the point of view of the group.

The two best-known **complex cyanides** are potassium ferro- and ferri-cyanide,  $K_4Fe(CN)_6$  and  $K_3Fe(CN)_6$ . The former is regarded as a compound of 4 KCN and  $Fe(CN)_2$ , and the latter of 3 KCN and  $Fe(CN)_3$ . Whilst, however, the former contains ferrous iron and the latter ferric, the iron cannot in either case be separated by precipitation, as in the case of ordinary ferrous and ferric salts. These compounds are not therefore double salts, like the alums, for instance, which separate more or less into their components in solution, but salts of potassium combined with the complex radicles  $^{IV}Fe(CN)_6$  and  $^{III}Fe(CN)_6$  respectively. The acids themselves,  $H_4Fe(CN)_6$  and  $H_3Fe(CN)_6$ , can be obtained by the suitable decomposition of their salts. When, therefore, ferrous and potassium cyanides combine together to form potassium ferrocyanide, a profound change takes place, by which a salt of complex constitution is produced, the iron ceasing to be a basic radicle and becoming a constituent of an acidic complex.

One of the best-known cobalt**ammines** is luteocobalt chloride, obtained by the oxidation of ammoniacal cobaltous chloride solution in presence of ammonium chloride. It is therefore a cobaltic derivative, and is represented by the formula  $Cl_3Co(NH_3)_6$ . Some analogy exists between this compound and potassium cobalticyanide,  $K_3Co(CN)_6$ , the difference being that whilst  $Co(CN)_6$  is a tribasic acidic radicle,  $Co(NH_3)_6$  appears to be a triacidic basic radicle.

An account will first be given of the complex cyanides and their allied compounds, and then of the metallic ammines, attention being drawn to such analogies as exist between them.

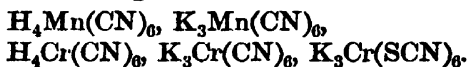
## COMPLEX CYANIDES

The following are the principal complex cyanides and their allied compounds:—

Types	$H_2RX_4$	$H_4RX_6$	$H_6RX_8$	$H_8RX_{10}$
Fe		$H_4[Fe(CN)_6]$ $K_4[Fe(CN)_6NO_2]$ $Na_4[Fe(CN)_6AsO_2]$ $Na_4[Fe(SCN)_6]$	$H_6[Fe(CN)_8]$ $K_3[Fe(CN)_8NO_2]$ $Na_3[Fe(CN)_8H_2O]$ $Na_3[Fe(CN)_8NH_2]$ $Na_3[Fe(SCN)_8]$	$H_8[Fe(CN)_{10}NO]$ $Na_2[Fe(CN)_{10}H_2O]$ $Na_2[Fe(CN)_{10}NH_2]$
Ni	$K_2Ni(CN)_4$			
Co		$H_4[Co(CN)_6]$	$H_6[Co(CN)_8]$ $K_3[Co(NO_2)_6]$	
Ru		$H_4[Ru(CN)_6]$		
Rh			$K_3[Rh(CN)_6]$	
Pd	$K_2Pd(CN)_4$ $K_2Pd(NO_2)_2Cl_2$			
Os		$H_4[Os(CN)_6]$		
Ir		$K_4[Ir(CN)_6]$	$H_6[Ir(CN)_8]$ $K_3[Ir(NO_2)_6]$	
Pt	$H_2Pt(CN)_4$ $K_2Pt(SCN)_4$			$K_2Pt(CN)_4Cl_2$ $K_2Pt(SCN)_6$ $H_2PtCl_4$

Where the acids themselves are known their formulæ are given.

Comparable with the above compounds, manganese and chromium form the following:—



And copper, silver, and gold the following:—



Likewise the members of Sub-group II B, zinc, cadmium, and mercury, form somewhat ill-defined double cyanides.

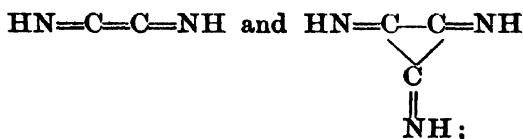
The complex or double cyanides in the above table present several stages of stability. The least stable are those of nickel and palladium, which, although they can be isolated in the solid state, are decomposed by dilute acids with separation of the simple cyanide. The most stable complex cyanides are those from which the complex acid itself may be isolated. Quite a number of these are known. The formula of the acid itself is given in the table, instead of that of its alkali salt, in

cases where the acid is stable and has been isolated.

It may again be pointed out, however, that no essential distinction, except in stability, can be drawn between double and complex salts, since all stages of stability exist between those compounds which are decomposed by water or dilute acids, as, for instance, potassium nickelocyanide, and those, such as potassium ferrocyanide, in whose aqueous solutions complex ions exist, and from which the free complex acids themselves can be prepared.

With the recognition of the existence of complex radicles containing cyanogen, arises the question as to their constitution.

It has been customary to regard these salts as derivatives of polymerized hydrocyanic acids,<sup>1</sup> such as



but such a view is not consistent with the relationship which obtains between this class of salts and the metallic ammines and analogous compounds. For example, consider the three compounds



It is fair to suppose that the two former bodies are of analogous constitution; and, as was suggested on p. 323,  $\text{K}_3\text{Co}(\text{NO}_2)_6$  and  $\text{Cl}_3\text{Co}(\text{NH}_3)_6$  are related to one another. Indeed the  $\text{NH}_3$  groups in the latter compound may be successively replaced by  $\text{NO}_2$  radicles, potassium taking the place of chlorine as the complex cobaltic radicle becomes acidic instead of basic, until finally  $\text{K}_3\text{Co}(\text{NO}_2)_6$  results. Moreover, as is shown in the table on p. 324, the complex cyanides themselves can exchange a CN group for another radicle or molecule, such as NO,  $\text{NO}_2$ ,  $\text{AsO}_2$ ,  $\text{H}_2\text{O}$ , or  $\text{NH}_3$ . Thus the view that the complex cyanides are derivatives of polymerised hydrocyanic acids is inadequate, because it does not admit of substitution of

<sup>1</sup> Browning, *Chem. Soc. Trans.* (1900), lxxvii, 1235.

other groups for a CN radicle, nor provide for the classification of these compounds with the large class of metallic ammines to which they are undoubtedly related. The theories which have been put forward regarding the constitution of the ammines will be considered in the sequel, so that for the present the constitution of the complex cyanides may be left undecided.

Of the compounds tabulated above, a few only of the most important can be considered here.

**Potassium ferrocyanide**,  $K_4Fe(CN)_6 \cdot 3H_2O$ . When potassium cyanide is added to ferrous sulphate solution, the red precipitate first formed dissolves when boiled with excess of the cyanide solution, forming a yellow liquid from which potassium ferrocyanide crystallises in quadratic pyramids. This salt was at one time prepared by heating iron with potassium carbonate and nitrogenous organic matter, but is now obtained from the cyanides produced in coal-gas manufacture.

**Hydroferrocyanic acid**,  $H_4Fe(CN)_6$ , itself separates as a white crystalline solid when hydrochloric acid is added to a concentrated solution of a ferrocyanide. Its ethyl ester possesses the molecular formula  $(C_2H_5)_4Fe(CN)_6$ .

When potassium ferrocyanide is added to excess of ferric salt, ferric ferrocyanide, or **insoluble Prussian blue**, having the empirical composition  $Fe_4[Fe(CN)_6]_3$  is precipitated.

If the ferrocyanide solution is slightly in excess of the iron, the precipitate consists of **soluble Prussian blue**, or hydrated ferric potassium ferrocyanide,  $Fe'''KFe(CN)_6$ . The so-called **Turnbull's blue**, obtained by precipitating  $\alpha$ . ferrous salt with ferricyanide solution, is found after washing to be identical with insoluble Prussian blue; thus it appears that ferrous ferricyanide, if at first produced, quickly undergoes intramolecular change into ferric ferrocyanide.

Indeed, it has been shown by Hofmann<sup>1</sup> that the blue compounds produced by precipitating ferric salts with ferrocyanide, by the oxidation of ferrous ferrocyanide, which is white, or by the reduction of ferric ferricyanide, which exists in solution as

<sup>1</sup> *Ann.* (1904), 337, 1; (1905), 340, 257.

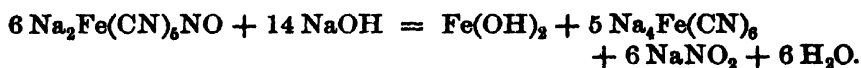
a brown compound, all conform to one or other of the formulæ,  $\text{Fe}'''\text{[Fe(CN)}_6\text{]}_3$  and  $\text{Fe}'''\text{XFe(CN)}_6$ , where X = hydrogen or an alkali metal.

The intensely blue colour of these compounds is attributed by Hofmann and Resenscheck<sup>1</sup> to the presence of both ferrous and ferric atoms within the same molecule.<sup>2</sup>

**The Nitroprussides.**—There remain to be considered compounds of the type  $\text{H}_2\text{RX}_6$ . The red salt  $\text{Na}_2[\text{Fe(CN)}_5\text{NO}] \cdot 2\text{H}_2\text{O}$ , known as sodium nitroprusside, is produced by the action of nitric acid on sodium ferrocyanide. It may be considered as sodium ferricyanide, in which NaCN has been exchanged for NO. Thus between hydroferricyanic acid and nitric oxide the following reaction takes place:—



The manner of decomposition of sodium nitroprusside with alkalis suggests, however, that the iron is present in the ferrous condition; thus:—



This substance is used as a reagent for alkali sulphides, with solutions of which it gives a purple colour. The compound thus produced is very unstable. Its composition may be represented by the formula  $\text{Na}_3[\text{Fe}''(\text{O}:\text{N} \cdot \text{SNa})(\text{CN})_5]$ .

Hydrogen sulphide itself is not sufficiently ionised in solution to react with nitroprusside.

In nitroprussides a (CN) group can be exchanged for  $\text{H}_2\text{O}$  or  $\text{NH}_3$ , as in compounds of other types.

#### AMMINES, OR AMMONIACAL COMPOUNDS OF THE METALS

It is well known that when ammonia is added to an aqueous solution of cupric sulphate, the basic sulphate which is at first

<sup>1</sup> *Ann.* (1906), 342, 364; (1907), 352, 54.

<sup>2</sup> The dark appearance which precipitated ferrous hydroxide assumes on partial oxidation supports this view, since the dark compound formed is hydrated  $\text{Fe}_3\text{O}_4 (= \text{FeO} \cdot \text{Fe}_2\text{O}_3)$ . Other examples of highly coloured substances which are compounds of lower and higher oxides of the same element are:

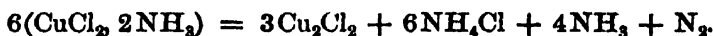
$\text{S}_2\text{O}_3$ ,  $\text{Pb}_3\text{O}_4$ ,  $\text{U}_3\text{O}_8$ ,  $\text{Mo}_3\text{O}_9$ .



precipitated dissolves in an excess of ammonia, forming a deep-blue liquid. From this liquid long prismatic crystals of cuprammonium sulphate,  $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$ , can be obtained by adding alcohol to the concentrated solution. Similarly, from cupric chloride crystals of the composition  $\text{CuCl}_2 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$  can be obtained. Both of these salts lose some ammonia when heated.

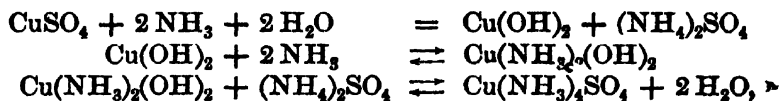
At  $150^\circ$   $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$  becomes  $\text{CuSO}_4 \cdot 2\text{NH}_3$ , and at  $200^\circ$   $\text{CuSO}_4 \cdot \text{NH}_3$ .

$\text{CuCl}_2 \cdot 4\text{NH}_3 \cdot 2\text{H}_2\text{O}$ , which is deep blue, yields the green compound  $\text{CuCl}_2 \cdot 2\text{NH}_3$  when moderately heated, and this at higher temperatures breaks up as follows:—

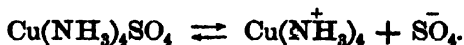


Further, anhydrous  $\text{CuCl}_2$  absorbs ammonia, forming  $\text{CuCl}_2 \cdot 6\text{NH}_3$ , whilst anhydrous  $\text{CuSO}_4$  forms the compound  $\text{CuSO}_4 \cdot 5\text{NH}_3$ . Cuprous chloride, as well as both cuprous and cupric oxide, also forms compounds with ammonia.

The constitution of these compounds can best be arrived at by a consideration of the properties of their solutions. Dawson and McCrae have shown<sup>1</sup> that when cupric oxide dissolves in ammonia a soluble base of the composition  $\text{Cu}(\text{NH}_3)_2(\text{OH})_2$  is produced, which undergoes partial electrolytic dissociation into  $\text{Cu}(\text{NH}_3)_2$  and  $\text{OH}$  ions, and further, that when ammonia is gradually added to a solution of cupric sulphate, the following changes probably take place:—



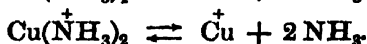
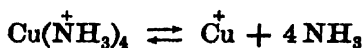
the cuprammonium sulphate thus produced dissociating electrolytically as follows:—



Probably some of the base  $\text{Cu}(\text{NH}_3)_2(\text{OH})_2$  also exists in the solution, together with its dissociated ions. These com-

<sup>1</sup> *Chem. Soc. Trans.* (1900), lxxvii. 1239.

pounds easily decompose with the evolution of ammonia, and this takes place in accordance with the following schemes:—



Ammonia is therefore intimately associated with the metal in these compounds; at the same time it appears to take the place of water of crystallisation in the compound  $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$ .

Compounds of analogous composition are probably produced in the case of cuprous oxide and chloride, as well as with zinc sulphate, cadmium iodide, and nickel sulphate.

Silver chloride forms with ammonia a solution, probably containing the compound  $\text{AgNH}_3\text{Cl}$ , and from which crystals of  $2\text{AgCl} \cdot 3\text{NH}_3$  can be obtained; and the oxide forms a solution containing  $\text{AgNH}_3\text{OH}$ , from which the nitride  $\text{Ag}_3\text{N}$ , known as fulminating silver, separates on exposure to air.

Zinc chloride forms several compounds with ammonia, the substance  $\text{ZnCl}_2 \cdot \text{NH}_3$  being so stable that it may be distilled without decomposition at a red heat. It is therefore:



#### AMMONIACAL COMPOUNDS OF THE EIGHTH GROUP, AND OF CHROMIUM

A very large number of these compounds are known.

The following are a few typical **cobaltammines** possessing characteristic colours:—

**Luteocobaltic**<sup>1</sup> chloride,  $(\text{NH}_3)_6\text{CoCl}_3$ , is obtained in reddish-yellow prisms when a solution of cobaltous chloride to which ammonium chloride and ammonia have been added is exposed to the oxidizing action of air, bromine, or lead peroxide. If ammonia only is added to cobaltous chloride, hydrochloric acid precipitates from such a solution after atmospheric oxidation **roseocobaltic** chloride,  $\text{H}_2\text{O}(\text{NH}_3)_5\text{CoCl}_3$ . When a solution of this substance in acid is warmed, **purpureocobaltic** chloride,  $(\text{NH}_3)_5\text{CoCl}_3$ , is precipitated. The radical ' $\text{NO}_2$ ' can replace

<sup>1</sup> Luteus = yellow.

chlorine from the above compounds. Thus from the purpureo salt the following substances may be produced by the action of nitrous acid:—

Croceocobaltic<sup>1</sup> chloride  $(\text{NH}_3)_5\text{CoCl}_2\text{NO}_2$ .

Xanthocobaltic<sup>2</sup> chloride  $(\text{NH}_3)_5\text{CoCl}(\text{NO}_2)_2$ .

Representative examples of cobaltammines and allied bodies are brought together in the following table, in which systematic nomenclature is adopted:—

*I. Compounds with a trivalent positive radicle.*

Hexammine cobaltic salts	$[\text{Co}(\text{NH}_3)_6]\text{X}_3$
Aquopentammine cobaltic salts	$[\text{H}_2\text{OCo}(\text{NH}_3)_5]\text{X}_3$
Diaquotetrammine cobaltic salts	$[(\text{H}_2\text{O})_2\text{Co}(\text{NH}_3)_4]\text{X}_3$
Triaquotriammine cobaltic salts	$[(\text{H}_2\text{O})_3\text{Co}(\text{NH}_3)_3]\text{X}_3$
Tetraquodiammine cobaltic salts	$[(\text{H}_2\text{O})_4\text{Co}(\text{NH}_3)_2]\text{X}_3$

*II. Compounds with a divalent positive radicle.*

Chloropentammine cobaltic salts	$[\text{ClCo}(\text{NH}_3)_5]\text{X}_2$
Bromopentammine cobaltic salts	$[\text{BrCo}(\text{NH}_3)_5]\text{X}_2$
Nitratopentammine cobaltic salts	$[\text{NO}_3\text{Co}(\text{NH}_3)_5]\text{X}_2$
Nitritopentammine cobaltic salts	$[\text{NO}_2\text{Co}(\text{NH}_3)_5]\text{X}_2$
Chloroaquotetrammine cobaltic salts	$[\text{ClH}_2\text{OCo}(\text{NH}_3)_4]\text{X}_2$
Chlorodiaquotriammine cobaltic salts	$[\text{Cl}(\text{H}_2\text{O})_2\text{Co}(\text{NH}_3)_3]\text{X}_2$
Chlorotriaquodiammine cobaltic salts	$[\text{Cl}(\text{H}_2\text{O})_3\text{Co}(\text{NH}_3)_2]\text{X}_2$

*III. Compounds with a monovalent positive radicle.*

1.6 Dichlorotetrammine cobaltic salts (praseo <sup>3</sup> )	$[\text{Cl}_2\text{Co}(\text{NH}_3)_4]\text{X}$
1.2 Dichlorotetrammine cobaltic salts (violeo)	$[\text{Cl}_2\text{Co}(\text{NH}_3)_4]\text{X}$
1.6 Dinitritotetrammine cobaltic salts (croce <sup>4</sup> )	$[(\text{NO}_2)_2\text{Co}(\text{NH}_3)_4]\text{X}$
1.2 Dinitritotetrammine cobaltic salts (flavo <sup>4</sup> )	$[(\text{NO}_2)_2\text{Co}(\text{NH}_3)_4]\text{X}$
Praseo-diethylenediammine cobaltic salts	$[\text{X}_2\text{Co}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_2]\text{X}$
Violeo-diethylenediammine cobaltic salts	$[\text{X}_2\text{Co}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_2]\text{X}$
Carbonatotetrammine cobaltic salts	$[\text{CO}_2\text{Co}(\text{NH}_3)_4]\text{X}$

<sup>1</sup> κρόκος = saffron.

<sup>2</sup> πράσινος = leek green.

<sup>3</sup> ξανθός = the colour of ripe corn

<sup>4</sup> flavus = golden yellow.



the radicle within the square brackets constituting a complex basic ion in the first three compounds, and an electrically neutral molecule in the fourth.

It will be observed, however, that the second and third formulæ suggest the possibility of a kind of isomerism; for instance, an alternative to the third compound would be  $[\text{Cl}(\text{NO}_2)\text{Co}(\text{NH}_3)_4]'\text{NO}_2$ . Cases of such isomerism have been observed<sup>1</sup>; the phenomenon is called ionisation-metamerism.

From the non-electrolyte  $[(\text{NO}_2)_3\text{Co}(\text{NH}_3)_3]$  the three  $\text{NH}_3$  molecules may be successively replaced by acidic radicles, so that the valency becomes negative; or, in other words, the molecular complex becomes an acidic instead of a basic radicle. For instance, the following potassium salts may be formulated:—



The first salt has a molecular conductivity at 1000 litres dilution of 99·29, comparable with 98·35 for  $[(\text{NO}_2)_2\text{Co}(\text{NH}_3)_4]'\text{Cl}$ ; the second salt is as yet unknown; the last salt is the familiar potassium cobaltinitrite.

The question now arises as to the relationship of the negative atoms or groups in these compounds to the cobalt atom, since they sometimes form part of the basic radicle, and sometimes constitute acidic radicles. This question is met by the hypothesis, which finds general acceptance, that when the negative atom or group is directly attached to the cobalt atom it is not capable of electrolytic dissociation, but forms part of a complex group, whereas when it is attached through a molecule of ammonia it undergoes electrolytic dissociation in solution, and constitutes an acidic radicle.

Thus, in the complex

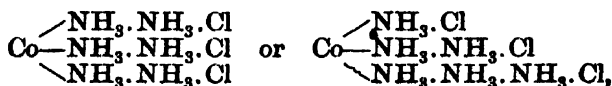


$\text{Cl}_{(\text{II})}$  is not ionised in solution, whilst  $\text{Cl}_{(\text{III})}$  is ionised. So the salts of cobaltammine bases may be regarded as substituted ammonium salts.

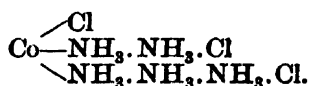
<sup>1</sup> Werner, Ber. (1907), 40, 84.

the salts of cobaltammine bases are regarded as substituted ammonium salts.

The valency of the cobalt atom remains, however, to be decided. It is possible to represent the constitution of, say,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  in such a manner as to show the cobalt to be trivalent, as by the formulæ:

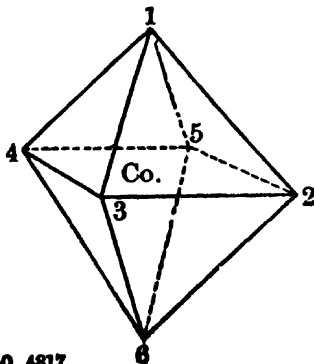


and then to represent a chlorine atom entering the basic complex according to the above principle as follows:—



This constitutes the theory of Blomstrand and Jörgensen. Werner, however, has shown that this view does not suffice to account for the remarkable properties of some of these compounds, to which attention must now be drawn.

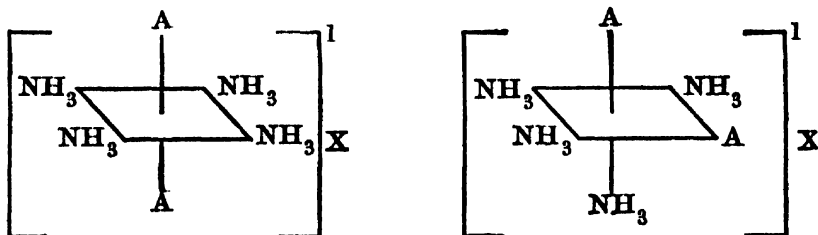
In the third group of compounds in the table, three cases of isomerism are quoted; the isomers differing chiefly in the colours of their salts. Thus, compounds of the type  $[\text{A}_2\text{Co}(\text{NH}_3)_4]\text{X}$  may be green or violet, and are known as praseo- and violeo-cobaltammines respectively. This phenomenon, first observed by Jörgensen, has been attributed by Werner<sup>1</sup> to stereoisomerism, that is, to a difference in the relative positions in space of the six groups around the central cobalt atom, which, together with this atom, constitute the basic radicle. According to Werner, these six atoms or groups lie at the six angular points of a regular octahedron, the cobalt atom being in the centre, thus:—



<sup>1</sup> Ber. (1907), 40, 4817,

It will be seen from an inspection of the figure that the positions 1 and 6 are similarly related to the central plane, whilst the positions 2, 3, 4, and 5 are similarly situated with regard to 1 or 6. Supposing, therefore, that position 1 is occupied by one of the two A atoms or radicles within the basic complex in the compound  $[A_2Co(NH_3)_4]X$ , the second A atom or radicle may be at 2 say, or at 6, and may thus give rise to two stereoisomers.<sup>1</sup> The remaining four positions will in each case be occupied by the four ammonia groups.

Thus Werner represents the isomerism of these compounds in the following way:—



This stereochemical theory further requires that with three acidic radicles within the basic complex, two isomers should be known in which the three radicles in question occupy the positions 1, 2, and 4, and 1, 2, and 3 respectively. The neutral compound  $[(NO_2)_3Co(NH_3)_3]$  is known in two isomeric forms, and thus further support is given to the theory.

Jørgensen<sup>2</sup> sought to account for the isomerism of the pairs of salts  $[(NO_2)_2Co(NH_3)_4]'X$  and  $[Cl_2Co(C_2H_4(NH_2)_2)_2]'X$  by assuming differences in the constitution of the  $NO_2$  radicles, and the arrangement of the ethylene-diamine molecules; but, apart from this, Werner<sup>3</sup>, having established the existence of two isomeric salts of the composition  $[Cl_2Co(NH_3)_4]'X$ , has justified the stereochemical formulæ.

Nevertheless, Werner has departed from the usual ideas of valency in thus accounting for these compounds. Indeed, he

<sup>1</sup> The A radicles might also be considered situated at 2 and 5, and 2 and 4 respectively; the result would be the same.

<sup>2</sup> *Zeit. Anorg. Chem.* (1897), **14**, 410, and (1899), **19**, 109.

<sup>3</sup> *Ber.* (1907), **40**, 4817.

assumes that two kinds of valencies exist—main valencies and auxiliary valencies. Main valencies are what are ordinarily understood by units of valency; when they are active the saturation capacities of the atoms exercising them are thereby diminished, and the basic or acidic radicles united by means of them are capable of ionisation in solution. Auxiliary valencies unite groups of atoms which cannot separately become ions, and their existence does not diminish the number of main valencies of the atoms concerned.

Since water and ammonia molecules attached to the cobalt atom do not diminish the ordinary (tri-) valency of that atom, Werner assumes that these molecules are *co-ordinated* with the cobalt atom by means of auxiliary valencies; a theory which he extends to include double and complex salts and crystallohydrates.<sup>1</sup>

Finally, the following generalization with regard to the cobaltammines and analogous substances may be given.—

*The combining power of the basic radicle present in ammine and allied compounds is always found to be equal to the difference between the normal valency of the metal, and the number of acidic radicles already included within the complex group containing the metal.*

Ammines and analogous compounds formed by other metals may now be briefly mentioned. Of these, the most closely allied to the above are those of **chromium**, derived from chromic salts, among which are the following:—

Aquopentammine chromic salts, *e.g.*  $[\text{H}_2\text{O}(\text{NH}_3)_5\text{Cr}]^{+++}\text{Cl}_3$ .

Chloropentammine chromic salts, *e.g.*  $[\text{Cl}(\text{NH}_3)_5\text{Cr}]^{++}\text{Cl}_2$ .

Nitritopentammine chromic salts, *e.g.*  $[\text{NO}_2(\text{NH}_3)_5\text{Cr}]^{+}\text{Cl}_2$ .

Tetrathiocyanatodiammine chromites, *e.g.*  $\text{K}[(\text{SCN})_4(\text{NH}_3)_2\text{Cr}]$ .

It will be noticed that the same law applies to the formation of these chromic compounds as to the cobaltic ammines; and analogous phenomena of isomerism have also been observed<sup>2</sup>.

**Iridium** forms three classes of ammines, derived from iridious chloride,  $\text{IrCl}_2$ , from iridic<sup>o</sup> chloride,  $\text{IrCl}_4$ , and from the tri-chloride,  $\text{IrCl}_3$ , these latter being analogous to the ammines of cobalt and chromium.

<sup>1</sup> See *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*, by A. Werner, 1909.

<sup>2</sup> Pfeiffer, Ber. (1904), xxxvii, 4255.



All the remaining metals of the eighth group, with the remarkable exception of iron, form ammines, though only those of platinum need be described. Nickel salts form compounds with ammonia; but they are related to the copper ammoniacal compounds rather than to those of cobalt.

Platinum forms two well-defined series of ammines corresponding to the platinous and platonic salts.

The following series is derived from platinous chloride:—

Tetrammine platinous chloride	$[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$
Chlorotriammine platinous chloride	$[\text{ClPt}(\text{NH}_3)_3]\text{Cl}$
Dichlorodiammine platinum (two isomers)	$[\text{Cl}_2\text{Pt}(\text{NH}_3)_2]$
Potassium trichloroammineplatinite	$\text{K}[\text{Cl}_3\text{Pt}(\text{NH}_3)]$
Potassium (tetra)chloroplatinite	$\text{K}_2[\text{Cl}_4\text{Pt}]$

And the following from platonic chloride,  $\text{PtCl}_4$ :—

		Electric Con- ductivity.
Hexammine platonic chloride	$[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$	522.9
(Chloropentammine platonic chloride	$[\text{ClPt}(\text{NH}_3)_5]\text{Cl}_1$	—
Dichlorotetrammine platonic chloride	$[\text{Cl}_2\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$	228
Trichlorotriammine platonic chloride	$[\text{Cl}_3\text{Pt}(\text{NH}_3)_3]\text{Cl}$	96.75
Tetrachlorodiammine platinum	$[\text{Cl}_4\text{Pt}(\text{NH}_3)_2]_2$	approx. 0
Potassium pentachloroammineplatinate	$[\text{Cl}_5\text{PtNH}_3]\text{K}$	108.5
Potassium (hexa)chloroplatinate	$[\text{Cl}_6\text{Pt}]\text{K}_2$	256

In the first of these series the maximum number of ammonia molecules which can exist within the complex is four, and in the second six. It will be observed that the same law concerning the replacement of ammonia by acidic radicles obtains as with the cobalt ammines.

The well-known compounds, the chloroplatinites and chloroplatينات (platino- and platini-chlorides), are regarded as the limiting examples in the two classes of ammine compounds.

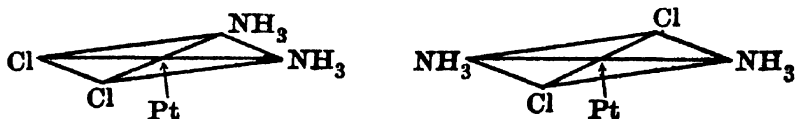
Finally, there must be considered the two pairs of isomers which these two classes of platinum ammines afford.

The non-electrolytic, neutral substance  $[\text{Cl}_2\text{Pt}(\text{NH}_3)_2]$  contains four groups attached to a central atom in two pairs. It is thus analogous to methylene chloride,  $\text{CH}_2\text{Cl}_2$ . This latter body, however, does not present any phenomenon of iso-

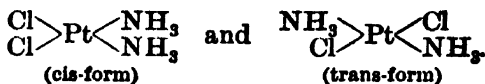
<sup>1</sup> Unknown.

<sup>2</sup> Two isomers.

merism, because the 4 atoms attached to the central carbon atom are equally distributed in space around it, as at the angular points of a regular tetrahedron. If, however, the 4 atoms or groups lay in one plane with the central atom, then isomerism would be possible. The isomerism of the above platinum compounds may be accounted for on this hypothesis, and their stereochemical formulæ may be constructed as follows:-



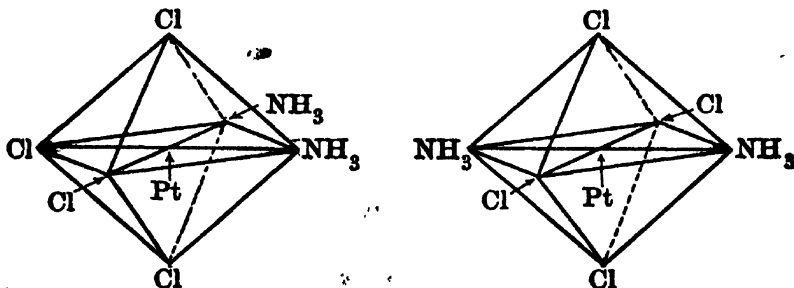
or more simply:



These two compounds, which have been studied by Werner, and whose geometrical isomerism is appropriately represented by the above formulæ, have been named respectively:

Chloride of platosemidiammine (cis-form) and  
Chloride of platosammine (trans-form).

If two negative groups, for instance two chlorine atoms, are added to each of the above compounds, so that platinic derivatives result, two more isomers are obtained—the tetrachlorodiammine platinum compounds:



These two bodies are analogous in their isomerism to the two dichlorotetrammine cobalt compounds.

## APPENDIX 1

## GROUP 0

## THE NON-VALENT ELEMENTS OF THE HELIUM GROUP

		Atomic weight.	Boiling-point at atm. press.	Melting-point.	Density of liquid.	At. vol. = at. wt. liq. dens.
Helium.....	He	3.99	-268.5	—	0.15	26.6
Neon.....	Ne	20.2	-233	—	—	—
Argon.....	Ar	39.88	-186.1	-189.6	1.40	28.5
Krypton...	Kr	82.9	-151.7	-169	2.155	38.5
Xenon.....	Xe	130.2	-109.1	-140	3.52	37.0

The discovery of these elements originated in an observation made by Lord Rayleigh in 1893, that atmospheric nitrogen is distinctly heavier than nitrogen obtained from chemical sources. It was at first thought that this discrepancy was due either to some isolated atoms among the diatomic molecules of chemical nitrogen which would make the gas lighter, or to the presence in the atmospheric gas of some condensed nitrogen molecules, say of  $N_3$ , which would account for the increased density.

Experiments were undertaken in conjunction with Sir William Ramsay, who suggested passing the purified atmospheric nitrogen over heated magnesium. Ordinary nitrogen would thus be absorbed, and any portion of the gas differing from the rest might remain. It was found that by this means the density of the gas was perceptibly increased owing to the removal of nitrogen, and finally a small volume of gas remained, the density of which exceeded 19. Rayleigh repeated the experiments of Cavendish, who had passed electric sparks through a mixture of oxygen and atmospheric nitrogen confined over weak potash solution. By this means Cavendish had actually obtained a small bubble of gas which could not be made to combine with oxygen, and Rayleigh confirmed his result. The spectrum of this gas, as well as that of the residue from

the magnesium absorption, differed from that of nitrogen or any known gas. Thus it appeared very probable that a new gaseous constituent of the atmosphere had been discovered. Further experiments made this conclusion certain, for it was shown that the proportion of the new gas in air could be increased by diffusion, and by solution in water, in which it is more soluble than nitrogen; and also that nitrogen obtained from sources other than the atmosphere left no residue when submitted to the action of red-hot magnesium or to the sparking process.

The new gas was called "**argon**", on account of its chemical inertness. This property is shown by the following facts. The gas fails to combine with oxygen, the halogens, or red-hot carbon, and also with metals such as magnesium. Attempts to oxidize it by the most powerful oxidizing agents proved fruitless. It enters into the chemical composition of no mineral, vegetable, or animal substance, though occurring in minute quantities in the occluded state in some rare minerals, and in solution in the water of certain springs.

• This failure to unite with any other element presented a new phenomenon in chemistry. Fluorine, indeed, does not combine with oxygen, but this is on account of its extreme electronegativeness; so that, with reference to hydrogen and the metals, it is the most active of the elements. Platinum and its allies, which always occur native, present the nearest approach to argon in chemical inactivity, though many compounds of platinum are known. It is now recognized that resistance to atomic union of all kinds is a characteristic property of argon; there is therefore no chemistry of this element. Further, since chemical union manifests valency, argon possesses no valency.

The question of molecular constitution and atomic weight next arises. Oxygen and nitrogen are known to consist of diatomic and mercury vapour of monatomic molecules, because the data concerning their density can be interpreted by atomic-weight determinations through chemical union. This method is not available for argon. The density of this gas is 19.8,

and its molecular weight, therefore, 39.88; its atomic weight has been determined by means of the following principle:—

It is known that the ratio of specific heat at constant pressure to that at constant volume is 1.4 for diatomic, and 1.66 for monatomic gases. This ratio for argon was found by Ramsay to be 1.659. Therefore argon is a monatomic gas, and its atomic weight is 39.88. The atoms of this element thus remain uncombined with one another in the gaseous state.

• An attempt to obtain argon from certain minerals, notably from cleveite, resulted in the discovery by Ramsay of another gas, which was found to shine with a pale-yellow light when excited electrically in a vacuum-tube. The spectrum of this gas was a brilliant one, and contained a yellow line identical in position with line  $D_3$  observed in the spectrum of the sun's chromosphere during the eclipse of 1868. This line had not previously been found in the spectrum of any terrestrial substance, and the element in the sun giving rise to it had been named "helium" by Lockyer.

In March, 1895, therefore, terrestrial helium was discovered. Besides cleveite, the minerals uraninite, bröggerite, and pitchblende yield this gas, together, sometimes, with argon; it has also been obtained from mineral springs, and is present in minute quantities in the atmosphere. The density of the gas is 1.995; it is monatomic, the ratio of the specific heats being 1.652; its atomic weight is therefore 3.99. It belongs to the same category as argon, since it combines with no other elements. Helium is less soluble in water than any other gas. Its boiling-point is  $4.5^\circ$  absolute. According to recent views,<sup>1</sup> to which reference will be made in the next appendix, this gas owes its origin in the above minerals to the breaking down into simpler constituents of some of the heavy atoms present.

• By experiments performed upon the liquefaction of the residual atmospheric gas, after absorption of nitrogen by magnesium,<sup>1</sup> or a mixture of this metal with lime, Ramsay and Travers made some further discoveries in the year 1898. "

<sup>1</sup> It has been shown by Soddy (*Proc. Roy. Soc.*, 1906, A. 78, 429) that strongly heated metallic calcium may be employed to separate the inert gases from the air, since it absorbs all gases possessing any chemical activity.

The gas was compressed in a bulb cooled to  $-185^{\circ}$  by immersion in liquid air. By this means most of the gas was liquefied, and on removal of the bulb from the liquid air its contents were separated into two constituents by rapid exhaustion. These fractions may be called (*a*) and (*b*). The (*a*) fraction, removed as gas, was cooled by immersion in liquid hydrogen, boiling at about  $-240^{\circ}$ . A portion of it solidified, and the remaining gas was found to be helium. The solid proved to be a new element of the argon family, to which the name "**neon**" was given. This element possesses a density of 10.1 and an atomic weight of 20.2, since it is monatomic. It is chemically inert, and gives an orange-red light in a vacuum-tube and a characteristic spectrum.

The fraction (*b*) contained argon, and two new constituents which are named respectively **krypton** and **xenon**. These were separated from one another by fractional distillation; the argon distilling first, krypton next, and xenon last, in accordance with their boiling-points, as given at the head of this chapter. Krypton and xenon resemble argon in the absence of chemical activity, and show characteristic spectra.

The relative proportions by volume of the minor constituents of the atmosphere are as follows:—

Argon	...	...	...	...	9330	parts	per	million.
Neon	...	...	...	...	12.3	"	"	
Helium	...	...	...	...	4.0	"	"	
Krypton	...	...	...	...	1.0	"	"	
Xenon	...	...	...	...	0.05	"	"	

So minute is the proportion of the last constituent that "it may be said with truth that there is less xenon in the air than there is gold in sea-water" (Ramsay).

## APPENDIX II

### THE PROBLEM OF THE ORIGIN OF THE ELEMENTS

Speculations as to the origin and transmutations of matter are as old as human thought. The four elements of the

ancients, earth, water, air, and fire, together with the quintessence of Aristotle, were conceived of, not as distinct material species in the modern sense, but as qualities of things which could change with changing circumstances. Thus water, representing the principles of moisture and coldness, could be changed by being heated into air, representing the principles of moisture and heat. The alchemists, who inherited the ideas of the ancient philosophers, attempted to apply them on a material basis; hence there arose the notion of a transmutation, not of properties, but of matter, and the quest for the philosopher's stone which should transmute base metals into gold. So far as the alchemists theorized concerning the nature of this supposed transformation, they believed it to be essentially an exceedingly slow natural process. Thus gold was supposed to grow by degrees, in mines, from common metal. The philosopher's stone, however, would greatly hasten the operations of nature, so as to reward the experimenter with an early crop of the precious metal. The evolutionary idea which underlies these notions appears not to differ in principle from present-day beliefs concerning material transformation; gold, however, is no longer regarded as the crown of elemental evolution, nor is it yet believed that human agency can influence the rate of such evolution.

Modern ideas of chemical evolution originated with Prout, who in 1815 put forward the suggestion that all the chemical elements are condensations of hydrogen. This suggestion was based upon the belief, which subsequent research dispelled, that the atomic weights, referred to that of hydrogen as unity, are whole numbers.

Notwithstanding the necessary abandonment of this belief, the fact remained that interesting relationships between the atomic weights and properties of certain elements could be traced. Döbereiner showed that various "triads" of allied elements exist, the properties and the atomic weight of the central member of a triad being the mean of those of the extreme members. This fact provided the germ of a system

of chemical classification of the elements; the beginning of the idea that allied species of elements are to be grouped in genera. This latter conception was much advanced by the law of octaves, and took permanent form in the periodic law.

The question then arose as to the connection between the classification of chemical species and the problem of the origin of such species; or, in other words, whether the periodic law might be taken as evidence of material evolution. Thus the underlying and ultimate question of all chemical science again recurred with increased emphasis; and, although the manner in which the periodic law might be supposed to afford evidence of chemical evolution was not at all clear, it was nevertheless generally accepted as an article of scientific faith, that the ultimate explanation of this great generalization would be found in a theory of the genesis of the elements from a common origin. It must however be stated that to the chief exponent of the periodic law, Mendeléeff, this deduction seemed unwarranted.

In 1887 Crookes gave an account of his researches upon the elements of the rare earths, in which he showed that there exist together in nature a number of bodies which are closely related, and which can only be separated so as to give evidence of distinct chemical identity, by very special and exhaustive means. And, just as the existence of different varieties of the same biological species suggests forcibly their derivation from a common stock, so the closeness of relationship in properties of the metals of the rare earths increases the probability that they are in some manner modifications of a common, original element. To the ultimate element from which by hypothesis all the different kinds of matter are derived, Crookes gave the name "protyle".

#### EVIDENCE OF SPECTRUM ANALYSIS

Evidence of inorganic evolution may, however, be sought in a wider field. When the spectroscope was brought into use by Bunsen and Kirchhoff, in 1859, and the significance of the dark lines in the solar spectrum, the so-called Fraunhofer



lines, was recognized, the science of cosmic chemistry began. The first work of the new science was the study of the chemistry of the sun; and it was shown that many terrestrial elements are present in our luminary, but that the sun also contains one or two elements which had not then been discovered upon the earth. With the perfecting of experimental methods, investigations spread to the distant stars and nebulae; until, by the accumulation of data, a classification of stars according to their chemical constitution was made possible. According to Sir Norman Lockyer, who has worked in this field, the results justify the doctrine of material evolution on a cosmic scale. Stars may be classified in the following two ways, amongst others: according to their temperature, and according to their material complexity.

The generalization arrived at by Lockyer states that with diminution of temperature there is an increase in material complexity. Further, in tracing the life-history of a star, it is recognized that after a certain maximum temperature has been reached—a condition produced by the aggregation and condensation of the original generating material—the subsequent history of the star is concerned with a gradual process of cooling, which continues until the star ceases to be visible. Therefore it may be concluded that elements come into existence in process of time which were non-existent in the earliest stages, when the star was hottest. Thus the familiar idea of material dissociation maintained by heat, and association occurring on cooling, finds an application in the widest cosmic phenomena.

The following chemical classification of stars is derived from the work of Lockyer:—

Gaseous stars	Hydrogen, helium, asterium	Highest temperature
Metallic stars	(a) Magnesium, calcium, silicon, oxygen	Medium temperature
	(b) Iron, manganese, nickel, copper, &c.	
Carbon stars	{ Carbon and compounds of carbon }	Lowest temperature.

The above may be considered a rough draft of a system of evolution of the chemical elements. It is interesting to observe that the order of appearance of the elements is approximately that of their material complexity as indicated by atomic-weight relationships. The case of carbon appears to be an exception to this rule; but although the atomic weight of carbon is low, there is reason to believe, on account of the non-volatility of the solid element,\*that its molecule at least is very complex. It is further interesting to observe that the one element especially essential to life appears amongst the last in the progress of inorganic evolution.

A further consideration related to this subject may be drawn from the domain of spectrum analysis. The spectra of the elements differ in degree of complexity. Thus the spectra of the alkali metals consist of few lines, whilst the spectrum of iron, for instance, contains a very large number. Can this latter substance indeed be an element, the atom of which vibrates in hundreds or even thousands of different ways at the same time, corresponding to the multitude of lines in its spectrum?

The question suggests a negative answer, and this in turn leads to an attempt to group and classify the lines of a complicated spectrum of a so-called element. This problem has been attacked by Balmer, Kayser, Runge and Paschen, and others.

It must first be observed that the nature of the spectrum of an element depends upon the temperature to which it is heated. The first effect of rise of temperature is the appearance of new lines. The flame spectrum of sodium, for instance, consists of two yellow lines very close together, and that of thallium of a single green line. The spark spectrum of sodium contains, in addition, a pair of lines in the orange, another in the green, and so on; whilst that of thallium contains, in addition to the green line, sets of bands in the violet. The interpretation which is given to this phenomenon is that the complete spectrum of an element obtained at the highest temperature is due to the vibrations

of matter in more than one state of atomic complexity; that the development of new lines, indeed, is caused by the dissociation of the supposed atoms of the element into various constituent parts, each of which manifests its own characteristic spectrum.

Support is given to this view by the establishment of numerical relationships between the wave-lengths of the lines of a spectrum; and also by a study of the magnetic perturbation of spectral lines.

**Numerical relationships of spectral lines.**—An examination of the spectra of such elements as nitrogen and carbon reveals the existence of “flutings” which occur at regular intervals throughout the length of the spectra. In the case of line spectra similar regularities have been observed. With lithium the complete spectrum consists of lines occurring singly; with sodium, copper, thallium, and silver, the lines occur in doublets; with magnesium, calcium, and zinc in triplets; whilst in the case of tin, lead, and bismuth, the groupings are more complicated. Further, not only do similar numerical groupings of lines repeat themselves throughout the spectrum of an element, but the particular relationships to each other of the individual lines in each grouping are reproduced.

Of the eleven triplets in the magnesium spectrum, the first three are given here in order to illustrate the above statement:

	$\frac{1}{\lambda}$	Difference
(i).....	{ 19290·7 .....	40·9
	{ 19331·6 .....	19·9
	{ 19351·5 .....	
(ii).....	{ 26052·2 .....	40·7
	{ 26092·9 .....	20·1
	{ 26113·0 .....	
(iii).....	{ 29968·6 .....	40·9
	{ 30009·5 .....	19·8
	{ 30029·3 .....	

A mathematical relationship has also been traced between the similarly situated lines of successive triplets, so that the

lines of the remaining triplets in the case of magnesium, for instance, can be calculated from a formula. This relationship has been worked out by Kayser and Runge.

The single lines of the hydrogen spectrum are also related to one another mathematically. Johnstone Stoney has shown that the three lines

$$H_{\alpha} = 6563.9 \times 10^{-7} \text{ mm.}$$

$$H_{\beta} = 4862.1 \times \quad \text{,,}$$

$$H_{\gamma} = 4102.4 \times \quad \text{,,}$$

are related to one another as harmonics of a single vibration, just as a single string gives a fundamental note and related harmonics; and that  $H_{\gamma} = 4339.5$  belongs to another series; and Balmer has calculated all the lines of the hydrogen spectrum from  $H_{\alpha}$  to  $H_{\gamma}$  from the formula

$$\lambda = A \frac{m^2}{m^2 - 4} \times 10^{-7} \text{ mm.},$$

where  $A$  is a constant  $= 3647.2$  and  $m = 3, 4, 5, \&c.$

The spectra of many so-called elements consist of more than one "series" of lines, and the question arises whether this fact affords evidence of material complexity. The spectrum of oxygen contains six series, the spectra of hydrogen, lithium, and sodium three each. The spectrum of helium has been shown by Runge and Paschen to consist of six series, and consequently the elementary nature of this gas has been called in question, some authorities attributing three series to the real helium and three to asterium.

It will be concluded from all this that related elements have analogous spectra. This is the case, and the atomic weights of certain elements have been calculated from the relationships of their spectra to those of allied elements of known atomic weights. For instance, Lecoq de Boisbaudran correctly estimated the atomic weight of germanium from such data; and the atomic weight of radium has similarly been calculated by Runge and Precht, though unfortunately a discrepancy exists between this value and that obtained by Madame Curie by chemical methods.

The evidence in this field is not extensive, but it appears that the relationships of the spectra of elements support the principle of periodic classification, and thus far contribute to the doctrine of material evolution.

**Magnetic perturbation of spectra.**—If a light source, giving rise to a spectrum, is placed in a strong magnetic field, the lines of the spectrum are observed to be "perturbed". This perturbation consists in a broadening, and more especially a division into doublets, triplets, or more complicated groups, of some or all of the lines which were previously single. The remarkable fact, however, is that different lines of the same spectrum are affected in different ways by the magnetic influence, and some are entirely unaffected; so that of a spectrum consisting originally of single lines, some of the lines give rise to doublets, triplets, quartets, and even sextets and octets, and others remain single. This modification of lines is due to the modification in the manner of vibration of the material particles at the light source, by the influence of the magnetic field; and the question arises whether particles of a single kind can have their mode of vibration modified in such an extraordinary manner, or whether the different kinds of changes induced in different lines of the spectrum correspond to different kinds of particles constituting the light source. The latter conclusion seems the more probable, and if it is accepted, the high temperature dissociation of the so-called atoms of the element in question into dissimilar particles necessarily follows.

A further point of interest is the fact that spectra of allied elements, such, for example, as magnesium, zinc, and cadmium, are similarly affected by magnetic influence; so that sets of lines can be discovered in each spectrum which undergo the same modification. This points to the important conclusion that the "atoms" of allied elements contain certain constituents in common.

**Fractionation.**—Brief reference was made on page 157 to the work of Sir William Crookes upon the fractionation of yttria. This is of special interest in connection with the

resolution of spectra into constituents. The "old yttria" of Crookes gave a definite phosphorescent spectrum *in vacuo*, and was long thought to be the oxide of a metallic element. By partial precipitation of an yttrium salt by less than an equivalent of ammonia, so that the more basic constituent remained in solution, Crookes obtained two fractions which differed very slightly in basic properties; and by repeating this process a great number of times, this chemist has divided the original yttrium into five or possibly eight constituents. Now each of these constituents gives a characteristic spectrum, and thus it is shown that the spectrum of a substance originally supposed to be an element is produced, not by similar, but by a number of dissimilar vibrating particles. So, from another point of view, spectrum analysis affords evidence of the complexity of the supposed atoms of matter.

#### RADIOACTIVITY

The evidence afforded by another field of research concerning the breaking down of the elements into simple constituents must now be considered. This branch of investigation originated previous to 1880, when Crookes commenced to study the phenomena of electric discharge through high vacua. The fluorescence of the glass of a "Crookes tube" containing a high vacuum, which is now recognized as the seat of origin of Röntgen rays, was explained by Crookes as due to the bombardment of the glass by particles of an attenuated form of matter, produced, as is now known, by the breaking down of the atoms of the gas originally contained in the tube into smaller constituent parts. Since they start from the cathode and travel in straight lines, these particles in motion are called **cathode rays**. Sir J. J. Thomson has shown that each of these particles is only  $\frac{1}{1836}$ th of the mass of an atom of hydrogen, and that they move with a velocity approaching that of light. It is significant that the final effect in the exhausted tube is independent of the nature of the gas originally present.

The particles likewise possess electrical properties, for not only are they deflected from their course by a magnet, but a

charge of electricity is found to accumulate on a receiver on which they impinge; further, they are able to pass through aluminium foil, and if the vacuum-tube is made of this metal, they will penetrate it and make their presence manifest in the external air, by exciting phosphorescence, by giving rise to certain electrical phenomena, and by acting on photographic plates.

These "corpuscles" of J. J. Thomson are believed to be units of negative electricity; in association with atoms of matter they constitute electrolytic ions; they have been called "**electrons**" by Johnstone Stoney. Thus the atomic structure of electricity is being recognized; and it has been pointed out by Thomson that the evidence in favour of such a view is similar to that which supports the atomic theory of matter, since a fixed quantity of electricity, or a simple multiple of this quantity, is always associated with an atom of matter in electrolysis.

Subsequently to the discovery of the Röntgen rays, other substances than glass, which fluoresce without electrical excitement, were examined, in order to discover if they emit rays. Research upon this subject has brought to light facts of much interest and significance, which constitute the new science of **radioactivity**.

First, it was found by Troost, Becquerel, and Arnold that certain phosphorescent bodies, such as calcium sulphide and hexagonal zinc-blende, emit rays which will act on a photographic plate after passing through aluminium foil 2 mm. thick. The salts of uranium, too, are well known to be fluorescent. Becquerel discovered that this fluorescence is connected with the emission of invisible "rays" which darken a photographic plate through aluminium foil.

There is, however, a difference between the phosphorescence of calcium sulphide and that of uranium compounds. For whilst the activity of calcium sulphide depends on the previous absorption of light, and therefore diminishes when the compound is kept for some time in the dark, that of uranium preparations is independent of the influence of light, and is

not lost even when the material is kept in the dark for a month. This property of "radioactivity" is possessed by various uranium minerals, such as pitchblende, bröggerite, and cleveite, to a greater degree than by uranium salts.

Pitchblende is a complicated mineral containing, besides uranium, barium, bismuth, and thorium, as well as other components; and the question arose whether the activity of uranium could be concentrated by the fractionation of its salts, or whether this property resided chiefly in some other component of the mineral, since the latter is more radioactive than the uranium salt prepared from it.

The concentration of radioactivity of uranium salt was achieved by Becquerel and Crookes. Becquerel found that on mixing barium chloride with a uranium solution and then precipitating the barium with sulphuric acid, and repeating this operation a number of times, the radioactivity was completely transferred to the barium sulphate, but that the residual inactive uranium regained its activity after eighteen months. This phenomenon suggested the idea that the acquirement of the property of radioactivity is connected in some way with a spontaneous change which uranium undergoes. Crookes separated from uranium salts by fractional crystallization a specially active constituent which he called "uranium X".

Even more striking results than the above were obtained by the investigation of the other constituents of pitchblende. Thus, in 1898, M. and Mme Curie fractionally crystallized barium halides obtained from pitchblende, and separated therefrom the less soluble halides of **radium**, a new element of the alkaline-earth family, whose radioactivity far exceeds that of uranium.

Similarly, the same observers isolated from the bismuth of the pitchblende another radioactive substance which they named **polonium**, and which is identical with Marckwald's radiotellurium.

Shortly afterwards Schmidt and Mme Curie proved that **thorium** and its compounds are radioactive; and in the follow-



ing year (1899) Debierne obtained another radioactive substance from the thorium of pitchblende, which he named **actinium**.

Most of the facts of radioactivity may be grouped round one or other of the three elements—radium, thorium, and actinium—and of these three the most interesting and important is radium.

The **chemistry of radium** and its compounds plainly corresponds with the position this element occupies as the highest member of the alkaline-earth group. The metal itself, which has been obtained by Mme Curie and Debierne,<sup>1</sup> is analogous in properties to barium, and its salts colour the non-luminous gas flame crimson. As would be expected, the chloride, bromide, and sulphate are less soluble than the corresponding barium salts (cf. pp. 119–120). The atomic weight of the element, determined by precipitating its chloride with silver nitrate, is 226·5.

The characteristic phenomena of radium, and of other radioactive substances, are connected with the emission of three kinds of radiation: the  $\alpha$ ,  $\beta$ , and  $\gamma$  rays, and with the evolution of radioactive gases.

Many chemical changes may be brought about by the action of the rays. Radium salts decompose water in which they are dissolved, and also bring about combination between hydrogen and oxygen; they also cause diamonds and other precious stones to phosphoresce and slowly change their colour. Glass tubes containing radium preparations become discoloured; this is probably due to the presence of colloidal metals produced from metallic ions liberated within the glass. Radium preparations confined within glass also effect chemical changes externally, such as the conversion of yellow into red phosphorus, the reduction of mercuric chloride by oxalic acid, the liberation of iodine from iodoform and from iodic acid, and the coagulation of globulin. These changes are brought about by the  $\beta$  and  $\gamma$  rays, which possess the power of readily penetrating glass.

The following provisional conclusions regarding the nature of the radium radiations may now be stated.

<sup>1</sup> *Compt. Rend.* (1910), 151, 523.

The  $\alpha$  and  $\beta$  radiations consist of minute particles emitted by the radioactive material with immense velocity. They are distinguished from each other by (i) their photographic activity, (ii) their power of penetrating layers of air or metal, (iii) their deviability in a strong magnetic field.

The  $\alpha$  rays are particles carrying double charges of positive electricity; each particle possesses four times the mass of a hydrogen atom. The velocity of the  $\alpha$  particles is upwards of 10,000 miles a second, and the phosphorescence of hexagonal zinc-blende in Crookes' *spinthariscopes* is due to their bombardment. These particles have little photographic activity, or power of penetrating air or aluminium foil; but, owing to the electric charge they carry, a gold-leaf electroscope is rapidly discharged in their presence.

The  $\beta$  rays are also particles. The mass of each is equal to about one-thousandth that of a hydrogen atom; their velocity varies, but may approach that of light (nearly 200,000 miles per second). These particles possess great photographic activity, and will pass through thin aluminium foil, though not through lead 1 cm. thick. In a magnetic field they are deviated a thousand times as much as the  $\alpha$  rays, and in the opposite direction. These properties recall those of the cathode rays, and it is recognized that the  $\beta$  particles are of the nature of high-velocity cathode rays, or electrons.

The  $\gamma$  rays possess about a hundred times the penetrating power of the  $\beta$  rays; they will even penetrate a lead shell 1 in. thick. They do not carry an electric charge, and are not deflected in a magnetic field, but, like Röntgen rays, they ionize gases, and so affect an electroscope, and also cause barium platinocyanide to phosphoresce. These rays are not particles,<sup>1</sup> but ethereal vibrations; and they consist of Röntgen rays of high penetrating power, produced by the agency of  $\beta$  rays, just as ordinary Röntgen rays result from the impact of cathode rays on glass.

In addition to these different kinds of "rays", radium,

<sup>1</sup> However, the view has recently been put forward by Bragg (*Phil. Mag.*, 1907 [vi], 14, 429) and others that the  $\gamma$  and X rays are corpuscular, consisting of neutral pairs of positive and negative electrons.

thorium, and actinium also "*emanate*" radioactive gases of transient activity, which, on account of their physical properties, appear to consist of definitely material particles.

The radium emanation may be described. It is best isolated by dissolving a radium salt in water in an evacuated flask. The evolved gases consist, besides the emanation, of water vapour, and of hydrogen and oxygen, produced by the action of the radium on water. After these gases have been eliminated, the emanation can be condensed by liquid air at about  $-155^{\circ}$ , and its vaporization with rise of temperature may be observed by the fluorescence of a neighbouring zinc sulphide screen. The passage of the emanation through a glass tube is made visible in the dark by the fluorescence of the glass. Diffusion experiments with the emanation prove it to have a density a little more than 100; and if it is a monatomic gas of the helium group, as appears likely, it is probably the last member of this group,<sup>1</sup> having an atomic weight of 222.5. The emanation possesses a characteristic spectrum.

The thorium emanation has similar properties, and is probably also a member of the helium family of gases. Radioactive gases have been extracted from deep wells by J. J. Thomson, and from the soil by Elster and Geitel. It appears that radioactivity may be manifested by many common substances, such as lead, wood, and brick, being induced upon inert matter by contact and by other means. The emanations of radium and thorium, for instance, can induce radioactivity on paper by contact; and Elster and Geitel found that a platinum wire to which had been given a powerful charge of negative electricity, collected radioactivity from the atmosphere, which, like a solid, could be dissolved from the wire by dilute acid, and deposited on a dish by evaporation of the acid.

So far it has been seen that the substance of radium continuously emits (i)  $\alpha$  and  $\beta$  particles, together with  $\gamma$  rays, (ii) a radioactive emanation.

It is necessary now to co-ordinate these facts, and to find some explanation of them.

<sup>1</sup> Ramsay has named the gas niton.

One explanation alone avails. These phenomena constitute a process of **atomic disintegration**, taking place in successive stages, which appear to be beyond human control, but have nevertheless been made known with a fair degree of completeness by the painstaking researches of workers in this field. External temperature conditions have no influence on these incessant changes, for they take place with the same rapidity between  $-180^{\circ}$  and  $1600^{\circ}$ .<sup>\*</sup> Moreover, they are accompanied by the evolution of heat energy, which was within the atom; so that, as was first shown by P. Curie and Laborde, a mass of radium salt continuously maintains itself at a temperature several degrees above that of surrounding objects.

Schweidler and Hess have shown that the amount of heat evolved is about 118 gram-calories per hour per gram of radium. Most of the heat comes from the emanation, through its further decomposition; and since, as will be shown later, the emanation has only a limited period of existence before it decomposes into something else, it is possible to estimate the total heat evolved during the "life" of a cubic centimetre of this gas, or in other words, the difference in energy content between the emanation and its first decomposition products.

This heat energy amounts to about seven million calories. An explosion of the same volume of electrolytic gas, which is the most powerfully exothermic chemical reaction known, would yield only three gram-calories, whence it follows that the heat of disintegration of the radium emanation produces more than two million times as much heat as any known chemical change.

Further particulars may now be given concerning the successive stages of disintegration of radium and similar elements.

It will be convenient to start with the radium and thorium emanations. It has already been observed that a solid disintegration product of some radioactive substance can be collected from the air by a negatively charged platinum wire. Rutherford found that a similar wire exposed to the thorium emanation became radioactive, and that this excited activity could be scraped off the wire or removed from it by hydro-

chloric acid. It appears, therefore, that the gaseous emanations of radium and thorium give rise to a solid disintegration product, for only a solid could be treated in such a manner.

Rutherford and Soddy believed that helium was also a disintegration product of the radium emanation, and identical with the  $\alpha$  particle; and Ramsay and Soddy showed that when the purified radium emanation is confined in a vacuum tube, its spectrum gives place after three or four days to that of helium. Thus for the first time was witnessed an authentic case of material transmutation; and an explanation was furnished also of the fact that terrestrial helium occurs only in radioactive minerals, whence it is evolved into the air.

The decay of the radium emanation thus consists in the loss of an  $\alpha$  particle which becomes an atom of helium; and the residue, which is solid, constitutes RaA. It has been shown that further changes quickly take place through RaC, RaD, RaE<sub>1</sub>, and RaE<sub>2</sub> to RaF, which is identical with polonium or Marekwald's radiotellurium. By one more radioactive change a permanent, inactive product is reached, which has an atomic weight of 206.5, and is believed to be identical with ordinary lead. Thus the history of radium ends in lead; but where does it begin? Is radium itself derived from some other element, known or unknown?

This question may be answered in part by reference to the known facts regarding the rate of disintegration of radium. The amount of emanation produced per unit time depends upon the amount of radium present at the time; and since this amount is constantly diminishing, the amount of emanation produced diminishes accordingly. It has been calculated from actual measurements of the emanation that in 1760 years a given quantity of radium will have reduced itself to one-half; therefore the half-life period of radium is said to be 1760 years.

An alternative expression to the half-life period is the period of average life. If  $\lambda$  is the fraction of an amount of a radioactive element which disintegrates in unit time,  $\frac{1}{\lambda}$  is

the average life period. Thus  $\frac{1}{2500}$ th part of radium disintegrates in a year, therefore the average life period of radium is 2500 years.

Now if all the radium in the earth's crust at the present time were only the remains of an original store of radium, in long past ages this store must have been very great. Considering the known rate of decay, it is estimated that at this rate the amount of radium 26,000 years ago would have been a million times, 52,000 years ago a billion times, 78,000 years ago a trillion times what it is now; and so, many thousands, but not millions of years ago, the earth must all have been radium. This is impossible, and therefore it cannot be believed that the radium now existing is the remains of a store that existed at the beginning. Consequently (if the possible alternative of the synthesis of radium from elements of lower atomic weight is dismissed) it follows that radium is the disintegration product of another element, which necessarily has a higher atomic weight than itself.

Now since radium is found in uranium minerals, and the atomic weight of uranium is higher than that of radium, it seemed natural to suppose that uranium is the parent of radium. The radioactivity of uranium salts was one of the earliest observed facts in the new science; but this activity is several million times less than that of radium; at the same time there is in pitchblende three million times as much uranium as radium. Now it is a necessary condition of radioactive equilibrium<sup>1</sup> that the specific rate of radioactive change is proportional to the concentration of the changing substance.

That uranium is the source of radium has been proved by Soddy and Mackenzie, who have detected the growth of radium in uranium freed from this element. The amount of radium found after a certain time was, however, much less than accorded with the ratio of the elements in pitchblende,

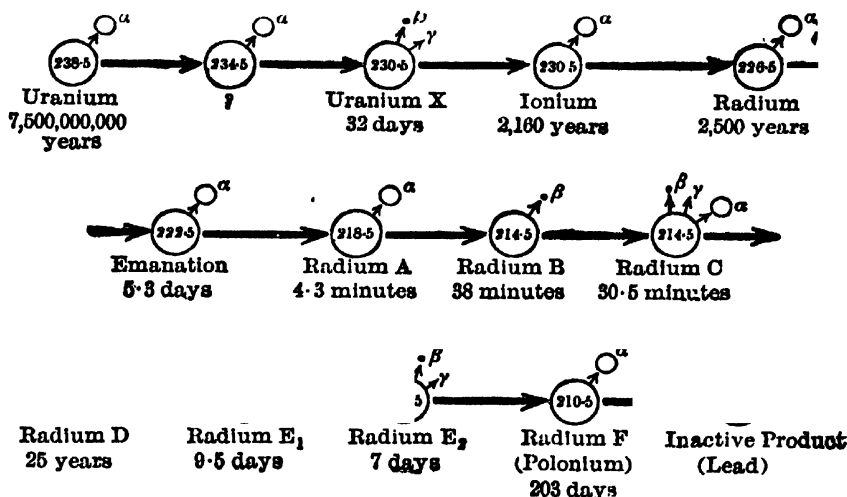
<sup>1</sup> Radioactive equilibrium is the state in which a radioactive substance is produced from other material at the same rate that it disintegrates, so that the total quantity of this substance remains constant.

Soddy illustrates the phenomena of successive radioactive changes by the water flowing through a series of reservoirs of different sizes (vide *The Interpretation of Radium*, p. 171, et seq.).

and this fact has led to the recognition of disintegration products intermediate between uranium and radium.

Thus uranium is the ancestor rather than the parent of radium, intermediate products being **uranium X**, previously recognized, and **ionium**.

The complete series of radioactive changes from uranium to lead may be represented graphically as follows, the average life period being stated under each product.



The relative quantities of radium and the succeeding disintegration products, derivable from a ton of uranium, which are directly proportional to their respective periods of average life, are shown in the following table:—

Period of Average Life.		Quantity.
Uranium,	7,500,000,000 years	1,000,000,000 mg. (= 1 ton).
Radium,	2500 years	333.3 mg.
Emanation,	5.3 days	One five-hundredth mg.
Radium A,	4.3 minutes	One millionth mg.
" B,	38 "	Nine millionths mg.
" C,	30.5 "	Seven " "
" D,	25 years	2.3 mg.
" E <sub>1</sub> ,	9.5 days	About four thousandths mg.
" E <sub>2</sub> ,	7 days	" " "
" F,	203 days	One fourteenth mg.

The above quantities are in radioactive equilibrium. On the water analogy they are represented by a series of reservoirs, through which a cascade of water flows, the contents of the reservoirs being in the ratio of these quantities.

Series of radioactive changes similar to the above have been observed with thorium and actinium. The results may be briefly stated as follows, the radiations lost being placed after each product:—

Thorium ( $\alpha$  rays)  $\rightarrow$  mesothorium 1 (rayless)  $\rightarrow$  mesothorium 2 ( $\beta$  and  $\gamma$  rays)  $\rightarrow$  radiothorium ( $\alpha$  rays)  $\rightarrow$  thorium X ( $\alpha$  rays)  $\rightarrow$  emanation ( $\alpha$  rays)  $\rightarrow$  thorium A ( $\beta$  rays)  $\rightarrow$  thorium B ( $\alpha$  rays)  $\rightarrow$  thorium C ( $\alpha, \beta, \gamma$  rays)  $\rightarrow$  inactive product (perhaps bismuth).

Actinium (rayless)  $\rightarrow$  radioactinium ( $\alpha$  rays)  $\rightarrow$  actinium X ( $\alpha$  rays)  $\rightarrow$  emanation ( $\alpha$  rays)  $\rightarrow$  actinium A ( $\beta$  rays)  $\rightarrow$  actinium B ( $\alpha$  rays)  $\rightarrow$  actinium C ( $\beta, \gamma$  rays)  $\rightarrow$  inactive product (nature unknown).

In the course of all these investigations about twenty-six transitional forms of matter have been recognized. Whether or not each of these different forms of matter, which are often evanescent to a degree, should be dignified by the name of element, is really a question of definition. Radium, however, is a member of the alkaline-earth series of metals, filling a hitherto blank space in the periodic scheme; therefore it is an undoubted element.

A few general considerations will bring this account of radioactivity to a close.

The radioactive substances hitherto described are the elements of highest atomic weight. Apart from these, the only elements showing any radioactivity are potassium and rubidium, and the phenomena presented by these metals are not yet understood.

So distinctly radioactive an element as uranium has an average life period of 7500 millions of years; and the life periods of elements which have not been observed to be radioactive must be immensely longer than that of uranium. It



is consequently impossible to set a limit to the average life period of the commonest terrestrial elements.

Atomic disintegration is accompanied by the disengagement of vast stores of internal energy; and uranium, having the heaviest atoms, possesses the most energy, which it loses in successive stages in its degradation into lead.

These considerations have several far-reaching consequences. Firstly, they have a distinct bearing on the ancient alchemistic problem of transmutation. Since the atom of gold is specifically lighter than that of lead, it is not *a priori* impossible that lead might yield gold by atomic disintegration, and at the same time furnish a large store of heat energy as a by-product. On the other hand, it is *a priori* impossible that silver should be transmuted into gold without the supply of such vast amounts of energy as would render the process economically valueless. As yet, however, there is no evidence whatever that atomic transformations of any kind can be initiated or controlled by human agency.

Secondly, the vast stores of energy which are contained within the atoms must have been absorbed during the formation of these atoms from the primal substance; and the disintegration of radioactive elements, which is known to be taking place, must be causing equally vast quantities of energy to be liberated. Consequently it is believed that the internal heat of the earth, and perhaps the maintenance of solar and stellar temperatures, are to be attributed to the disintegration of radioactive elements.

Thirdly, the smallest recognizably material particle produced by the breaking up of a radioactive element is an atom of helium. This is derived from the  $\alpha$  particle; but  $\beta$  particles are also produced, which are of several thousand times less mass than  $\alpha$  particles. These are electrons or atoms of electricity. As far as present knowledge goes, electrons are ultimate particles; and it remains a most remarkable fact that these same particles are produced as cathode rays when an electric discharge is passed through a high vacuum. Thus it appears that the basis of the material universe is electrical.

Through the study of the subjects gathered together in these pages some insight has been gained into the great problems of the origin and destiny of matter. What the complete manner of such material evolution and devolution may be is at present undisclosed; but it would appear that the periodic law must constitute a hieroglyphic whose final interpretation will afford a solution of the problem.

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*[The black figures give the chief reference among several.]*

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